ESL-TR-86-66
VOL I

(2)

EVALUATION AND PREDICTION OF HENRY'S LAW CONSTANTS AND AQUEOUS SOLUBILITIES FOR SOLVENTS AND HYDROCARBON FUEL COMPONENTS
VOL I: TECHNICAL DISCUSSION

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SEPTEMBER 1987

FINAL REPORT

FEBRUARY 1985 - SEPTEMBER 1986

AFESC

ENGINEERING & SERVICES LABORATORY
AIR FORCE ENGINEERING & SERVICES CENTER
TYNDALL AIR FORCE BASE, FLORIDA 32403

UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved OMB No 0704-0188

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b RESTRICTIVE MARKINGS N/A
2a SECURITY CLASSIFICATION AUTHORITY N/A	3 DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release. Distribution Unlimited
2b DECLASSIFICATION/DOWNGRADING SCHEDULE N/A	
4 PERFORMING ORGANIZATION REPORT NUMBER(S)	5 MONITORING ORGANIZATION REPORT NUMBER(S) ESL-86-66
6a NAME OF PERFORMING ORGANIZATION Research Triangle Institute 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION HQ AFESC/RDVW
6c ADDRESS (City, State, and ZIP Code) P.O. Box 12194 Research Triangle Park NC 27709	7b ADDRESS (City, State, and ZIP Code) Tyndall AFB FL 32403
8a NAME OF FUNDING/SPONSORING ORGANIZATION Same as Block 7 8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F08635-85-C-0054
8c ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO: 62601F; PROJECT NO: 1900; TASK NO: 70; WORK UNIT ACCESSION NO: 29

11 TITLE (Include Security Classification)
Evaluation and Prediction of Henry's Law Constants and Aqueous Solubilities for Solvents and Hydrocarbon Fuel Components

12 PERSONAL AUTHOR(S)
Howe, G.B.; Mullins, M.E.; Rogers, T.N.

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Final	FROM Feb 85 TO Sep 86	September 1987	98

16 SUPPLEMENTARY NOTATION
Availability of this report is specified on reverse of front cover.

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Volatile organics, solvents, fuels, Henry's law constants, aqueous solubilities, air/water distribution.
07	01		
07	04		

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

Laboratory measurements of Henry's law constants are reported for 51 chemicals, spanning a wide range of chemical structures and volatilities. A static headspace method (Equilibrium Partitioning in Closed Systems, referred to as EPICS) was used to measure Henry's Law Constant, with the standard batch air-stripping method used as a check. An average precision of 5 percent was obtained for the EPICS runs, and the Henry's law constants agreed reasonably well (within 10 percent) with the batch air-stripping results and other reported experimental values. Measurements were conducted over a temperature range of 10-30°C, and the data were correlated with a temperature regression equation coupled with a temperature-dependent error term based on 95 percent confidence limits. The aqueous solubilities of the study compounds were also determined via the shake-flask method at temperatures of 10, 20, and 30 degrees Celsius. Finally, the results of this study were incorporated into a thermodynamic correlation (UNIFAC), based on chemical structure, which allows the prediction of Henry's law constants and aqueous solubilities for a wide variety of pure compounds and mixtures (Cont'd)

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION
22a NAME OF RESPONSIBLE INDIVIDUAL	22b TELEPHONE (Include Area Code) 22c OFFICE SYMBOL

DD Form 1473, JUN 86 Previous editions are obsolete

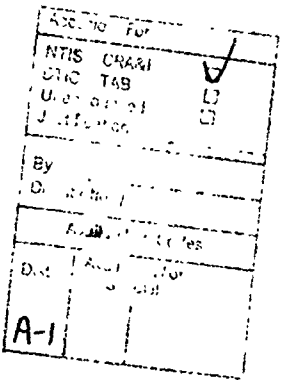
Keywords:

SECURITY CLASSIFICATION OF THIS PAGE
UNCLASSIFIED

ITEM 19. ABSTRACT (Cont'd)

in dilute aqueous solutions. Volume I. Technical Discussion Volume I of III

This report is presented in three volumes. Volume I contains the technical discussion and fabulated values of Henry's law constants and aqueous solubilities. Volume II contains the experimental Henry's law data. Volume III contains the experimental solubility data and the FORTRAN source code for the simples UNIFAC parameter fitting and the interactive program for calculating Henry's law constants and aqueous solubilities.



EXECUTIVE SUMMARY

The Installation Restoration program (IRP) underway at numerous Air Force bases has identified several sites with contaminated soil and groundwater. This subsurface contamination is the result of fuels, cleaning solvents, and degreasers entering the subsurface environment from accidental spills, leaking storage tanks, and past disposal practices. HQ AFESC/RDVW is conducting research aimed at developing treatment strategies for groundwater cleanup, and studying the fate and transport of contaminants in subsurface systems. Many of the contaminants of concern are volatile by nature, and a knowledge of their air-water distribution and aqueous solubility is needed to assess the compounds' treatability and to support the basic laboratory studies.

The objectives of this research were to develop Henry's law constants and aqueous solubilities as a function of temperature, for a variety of organic compounds of Air Force concern (Table 1). Secondary objectives were to determine what effect mixed organics, in an aqueous solution, exhibit on individual Henry's law constants and evaluate various methods used to predict Henry's law constants.

This report documents experimentally determined values of Henry's law constants and aqueous solubility for 51 compounds of Air Force concern. The report is presented in three volumes. Volume I contains the technical discussion and tabulated values of Henry's law constants and aqueous solubilities. Volumes II and III contain all the raw data and the FORTRAN source code for an interactive program used to predict the chemical parameters.

Many of the contaminants of concern are volatile by nature, and a knowledge of their air-water distribution is required for the design of treatment processes and for providing insight into their environmental fate and transport. A static headspace method (Equilibrium Partitioning In Closed Systems, referred to as EPICS) was used to measure the Henry's law constants, with the standard batch air-stripping method used as a check.

The Henry's constants were determined as a function of temperature from 10 to 30 ^{o}C (Table 11) and these values were then used to generate temperature regression equations (Table 8). Generally speaking the EPICS' results from this study agree well with other published results (Table 12). However, for many of the compounds reported here, confirmed values of Henry's constant do not exist in the literature, and, if they do, values are rarely reported as a function of temperature with rigorous statistics.

Solubility data for organic compounds in water are important for environmental studies because they provide fundamental information necessary to predict transport in aqueous systems. These data may also be used to predict carbon sorption of contaminants, and the air- or steam-stripping behavior for a given compound. The aqueous solubilities of the 51 study

compounds were determined at 10, 20, and 30°C (Table 14). Three different methods were used, but the majority of the data were collected using a shake-flask technique. Although the solubilities were not a strong function of temperature over the range studied (i.e., 10-30 °C), several general trends were noted. First, the solubility of the halongenated hydrocarbons increased with temperature. Second, the solubility of the substituted aromatic hydrocarbons increased with temperature. Finally, maxima and minima were observed for a wide range of compounds without any general trend that can be demonstrated to be statistically significant.

Groundwater contamination is often characterized by the presence of several different contaminants, rather than one single compound. For this reason, studies were conducted to determine whether the presence of other compounds would affect the Henry's law constant of a single compound. Deviations from ideal behavior were observed (pg 52), but confirming experiments were not performed. Although the results were not conclusive, the project team believes the observed interactions were real and reproducible.

It would not be feasible to experimentally determine Henry's law constants for all chemical compounds. There will be times when a Henry's law constant is needed but an experimentally determined value is not reported and the situation does not permit a laboratory study to determine the constant For this reason, a technique to accurately estimate Henry's constant using a minimum of physiochemical properties would be useful. Three different thermodynamic techniques for correlating experimental Henry's law constants were examined (page 61). The techniques were examined to determine their applicability to environmental systems and their predictive capacity for unmeasured multicomponent systems. The UNIFAC method proved to be the most effective way of utilizing the data base developed during this project. A computer algorithim to fit the current data to a new environmental UNIFAC binary interaction data base was developed and a portion of the experimental data collected was incorporated into this new data base. The new data base creates improvement in the predictions generated by UNIFAC in the dilute concentration regime (Figures 13 through 16).

PREFACE

This report was prepared by the Research Triangle Institute, Research Triangle Park NC 22707, under Contract No. F08635-85-C-0054. The AFESC/RDVW Project Officer was Captain Richard A. Ashworth.

The report documents Henry's law constants and aqueous solubilities, as a function of temperature, for 51 compounds of Air Force concern. The study was performed between February 1985 and September 1986.

This report is presented in three volumes. Volume I contains the technical discussion and the tabulated values of Henry's law constants and aqueous solubilities. Volume II contains the experimental Henry's law data. Volume III contains the experimental solubility data and the FORTRAN source code for the simplex UNIFAC parameter fitting and the interactive program for calculating Henry's law constants and aqueous solubilities.

Mention of trademarks and trade names of material and equipment does not constitute endorsement or recommendation for use by the Air Force, nor can the report be used for advertising the product.

This report has been reviewed by the Public Affairs Office (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

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SECTION I

INTRODUCTION

A. OBJECTIVE

The objectives of this research effort are to develop Henry's constants and aqueous solubilities as a function of temperature for a variety of organic compounds of Air Force concern. Secondary objectives are to determine what effect mixed organics in an aqueous solution exhibit on individual Henry's Law constants and to correlate changes in chemical structure with Henry's constants. Fifty-one chemicals of interest to the Air Force for evaluation of air-stripping technology were examined. The results are presented in this report in considerable detail, and the methodology for development of a chemical correlation is developed.

B. BACKGROUND

The current Installation Restoration Program (IRP) underway at numerous Air Force bases has identified several groundwater contamination sites. These contaminants are the result of fuels, cleaning solvents, and degreasers entering the groundwater from past disposal practices, accidental spills, and leaking storage tanks. The Air Force is currently conducting an active research program to investigate feasible treatment strategies for groundwater cleanup and to study the interactions between groundwater pollutants and soils.

Packed tower air-stripping is one of the treatment strategies being developed by the Air Force and has proven to be an excellent technique for removing trichloroethylene from groundwater. The same technique should be applicable to other volatile organic compounds, but pilot-scale testing is needed to verify system designs. Accurate values of Henry's law constants are critical in obtaining reliable design data. Rarely will a single compound be the sole contaminant found in groundwater. Groundwater contamination is usually characterized by the presence of several of these compounds. For this reason, studies are needed to identify what effect complex mixtures may have on the individual Henry's law constants for single components.

Henry's law constants have been estimated for many compounds frequently using chemical property data which are suspect. Until experimentally determined Henry's constants are available, other Henry's law constants should be used with caution. In the past, most Henry's law constants were experimentally determined using a bubble-purge technique that is theoretically valid. However, the technique requires numerous assumptions to be practically applied. For this reason, Dr. J. Gossett and A. Lincoff (Reference 1) developed a new method to determine Henry's law constants while working on an Air Force sponsored research project. The method, called Equilibrium Partitioning In Closed Systems (EPICS), uses relative headspace concentration from two equilibrated systems to determine Henry's law constants.

It is not feasible to experimentally determine Henry's law constants for all chemical compounds. There will be times when a Henry's law constant is needed but an experimentally determined value is not reported and the situation does not permit a laboratory study to determine the constant. As mentioned earlier, techniques currently used to estimate Henry's law constant, such as the ratio of vapor pressure to solubility, have inherent limitations that restrict their use. For this reason, a Henry's law constant correlation based on a minimum of physiochemical properties would be useful. It is, therefore, desirable to correlate chemical structure with changes in Henry's law constant for the organic compounds of interest in this study, to determine how structural differences may influence equilibrium partitioning.

The Air Force is also conducting studies aimed at determining the partitioning and transport of volatile compounds in groundwater systems. The transport of contaminants in groundwater systems is often controlled by the sorption between the contaminant in question and the surrounding aquifier materials. Contaminant aqueous solubility is an important property used to estimate sorption equilibria. However, accurate solubility data are scarce and compounds are often simply reported as soluble, slightly soluble, or insoluble. For this reason, solubilities determined as a function of temperature for each chemical will support sorption studies. The determination of accurate Henry's law constants will also support these studies providing reliable data which can be used in developing useful mass balances for chemical partitioning.

C. SCOPE

A comprehensive literature survey was performed to obtain Henry's law constants and aqueous solubilities for each chemical listed in Table 1. The literature values are compared with the results of the research effort and included in this final report.

Henry's law constants were then determined for all the chemicals listed in Table 1 using the EPICS technique when applicable. Although the EPICS technique has proven to be a simple and accurate method for Henry's constant determination, the EPICS method is reported to lose utility when the dimensionless Henry's law constant is greater than two or three. Therefore, the bubble column method was used to determine Henry's constants for several chemicals for comparison to the EPICS technique. The purpose of this alternate measurement was to verify the measured Henry's law constants.

Henry's law constants for each chemical listed in Table 1 were determined as a function of temperature at 10, 15, 20, 25, and 30 degrees Celsius. In addition, the aqueous solubilities for each chemical listed in Table 1 were determined as a function of temperature at 10, 20, and 30 degrees Celsius.

TABLE 1. LIST OF STUDY COMPOUNDS

Number	Component name
1	n-Nonane
2	n-Hexane
3	2-Methylpentane
4	Cyclohexane
5	1,2-Dichlorobenzene
6	Chlorobenzene
7	1,3-Dichlorobenzene
8	1,4-Dichlorobenzene
9	o-Xylene
10	p-Xylene
11	m-Xylene
12	Propylbenzene
13	Ethylbenzene
14	Toluene
15	Benzene
16	Phenol
17	Methyl ethylbenzene
18	1,1-Dichloroethane
19	1,2-Dichloroethane
20	1,1,1-Trichloroethane
21	1,1,2-Trichloroethane
22	cis-Dichloroethylene
23	trans-Dichloroethylene
24	Tetrachloroethylene
25	Trichloroethylene
26	Naphthalene
27	Tetralin
28	Decalin
29	Anthracene
30	Vinyl chloride
31	Chloroethane
32	Hexachloroethane
33	Carbon tetrachloride
34	1,3,5-Trimethylbenzene
35	bis(2-Ethylhexyl) phthalate
36	Ethylene dibromide
37	1,1-Dichloroethylene
38	Methylene chloride
39	Chloroform
40	1,1,2,2-Tetrachloroethane
41	1,2-Dichloropropane
42	Dibromochloromethane
43	1,2,4-Trichlorobenzene
44	2,4-Dimethylphenol
45	1,1,2-Trichlorotrifluoroethane
46	Methyl ethyl ketone (MEK)
47	Methyl isobutyl ketone (MIBK)
48	Methyl cellosolve
49	bis(2-Chloroethyl) ether
50	Trichlorofluoromethane
51	2,6-Dinitrotoluene

An attempt was also made to evaluate the effects of mixed organics in aqueous solutions on individual Henry's law constants. Based on information obtained for pure components, six compounds, selected from Table 1, were expected to cause the greatest amount of deviation in individual Henry s law constants. The Henry's law constants for each compound in the mixture were determined and the results were compared to the pure component Henry's law constants determined previously.

The final goal of this study was to derive a correlation to predict Henry's law constant based on a knowledge of the chemical structure of the compound in question. Two approaches have been investigated: an extension of the UNIFAC solution of groups model as proposed by Fredenslund, et al. (Reference 3); and the parent-derivative method of Leo, Hansch, and Elkins (Reference 4). Once the method is fully developed, the applicability of the correlation may be demonstrated by selecting five chemicals and predicting their respective Henry's law constant. The predicted Henry's law constants can then be compared to laboratory values determined earlier. The correlation resulting from these efforts is relatively simple to apply, requires a minimum of physiochemical properties, and is adaptable to other hydrophobic chemicals and mixtures not examined in the current research effort.

SECTION II

A REVIEW OF HENRY'S LAW CONSTANT CRITERIA

Air and water contamination by volatile organic compounds (VOCs) has become a major environmental concern in the United States, as evidenced by the intensive monitoring and regulatory activities of recent years. Current VOC contamination problems include air emissions from hazardous waste treatment, storage, and disposal facilities (TSDFs) and groundwater contamination by leaking underground fuel storage tanks. In these and other cases, a knowledge of VOC-air-water equilibrium behavior is critical in designing VOC handling and treatment processes that minimize environmental impact. Because the VOCs are usually present in the liquid phase at very low concentrations, Henry's law for ideal dilute solutions is often appropriate for vapor-liquid equilibrium (VLE) calculations.

The ongoing VLE program includes the laboratory determination of Henry's law constants and aqueous solubilities for hydrophobic organic chemicals. State-of-the-art techniques are being employed for these measurements, and the precision and accuracy of the data are monitored by a variety of statistical tests.

A. THEORETICAL SOLUTION THERMODYNAMICS

The governing equation for the equilibrium partitioning of component "i" between a liquid and a vapor phase in contact is simply:

$$\hat{f}_i^V = \hat{f}_i^L \qquad \text{(at equilibrium)} \tag{1}$$

where

$\hat{f}_i^V$ = fugacity of component "i" in the vapor mixture.

$\hat{f}_i^L$ = fugacity of component "i" in the liquid mixture.

It is not convenient to work directly with fugacities, so the following expressions are usually introduced to relate physically measurable quantities in the two phases at equilibrium:

$$\hat{f}_i^V = Y_i \hat{\phi}_i P \tag{2}$$

$$f^L = X_i \gamma_i f_i^o \quad (3)$$

where

Φ_i = fugacity coefficient (equal to unity if the vapor behaves as an ideal gas)

γ_i = activity coefficient (equal to unity for an ideal solution)

X_i, Y_i = mole fractions of "i" in the liquid and vapor phases, respectively

f_i^o = standard state fugacity of "i".

Using Equations (2) and (3) and assuming ideal vapor and liquid phases, the result is:

$$Y_i P = X_i f_i^o \quad . \quad (4)$$

To apply this equation, the standard state (f_i^o) must be chosen judiciously, based upon the liquid-phase composition of the system. Henry's law behavior arises when the liquid mixture of interest is very dilute in component "i" and a direct proportionality is observed between the fugacity of "i" and its mole fraction in the liquid phase. Thus, f_i^o becomes equal to the Henry's constant, H_i, which is defined by the relationship:

$$H_i = \lim_{X_i \to 0} \left(\frac{f_i}{X_i}\right) = \lim_{X_i \to 0} \left(\frac{Y_i P}{X_i}\right) \quad (5)$$

where

P = total system pressure, atm.

For Raoult's Law behavior when the liquid mixture is almost pure component "i", the standard state becomes the pure component vapor pressure (P_i^{sat}). At infinite dilution, the Raoult's law relationship becomes:

$$Y_i P = X_i \gamma_i^{\infty} P_i^{sat} \quad (6)$$

where

γ^{∞} = the infinite dilution activity coefficient

P_i^{sat} = the pure component vapor pressure.

Comparing Equations (4) and (6), Henry's law constant is equivalent to the product of the infinite dilution activity coefficient and the pure component vapor pressure:

$$H_i = \gamma_i^{\infty} P_i^{sat} \quad . \tag{7}$$

Hence, by knowing the pure component "i" vapor pressure and the Henry's law constant at any given temperature, one may calculate the infinite dilution activity coefficient at that temperature.

B. UNITS CONVERSION FOR HENRY'S LAW CONSTANT

The Henry's law constant in Equation (5) has thermodynamic units [(atm)(kmols of liquid)/(kmols of gas)] and can be converted to dimensionless form by multiplying by the ratio of the molar gas and liquid densities. This second form of Henry's law is useful for relating the aqueous concentration of a hydrophobic organic compound to its equilibrium concentration in the vapor phase:

$$C_G = H_i' C_L \tag{8}$$

where

C_G = molar concentration of organic in the gas phase, g moles/m^3

C_L = molar concentration of organic in the liquid phase, g moles/m^3

H_i' = dimensionless Henry's law constant.

A third form of Henry's law is often used, and the Henry's constant can be expressed in still another set of units. The phase equilibrium expression in this case relates the liquid-phase concentration of "i" to its partial pressure in the vapor phase:

$$P_i = Y_i P_T = H_i'' C_L \tag{9}$$

where

P_i = partial pressure of "i," (atm)

Y_i = mole fraction of "i" in the vapor phase.

Solving for Henry s law constant, H_i'', gives the following equation and associated set of units:

$$H_i'' = \frac{Y_i P_T}{C_L} \equiv \left[\frac{\text{atm } (m^3 \text{ of liquid})}{(\text{kmols of gas})}\right] \quad . \tag{10}$$

In summary, the required conversion equations between the three different sets of units for Henry's law constant are:

$$H_i = H_i' \frac{\rho_L}{\rho_G} = H''(\rho_i'')_L \tag{11}$$

or

$$H_i' = H_i''(\rho_G) \quad . \tag{12}$$

All constants in the text of this report are in the form of Equation (10). However, notice that pressure units of both kilopascals (kPa) and atmospheres (atm) are employed for the sake of scaling or comparison to other reported data. The unit conversion between the two is simply 101.325 kPa/atm. Appendix B list the Henry's law constants in many sets of units and in dimensionless form.

C. TEMPERATURE DEPENDENCE OF HENRY'S LAW CONSTANT

From fundamental thermodynamic relations, the temperature and pressure dependence of Henry's law constant can be shown to be

$$d(\ln H_i) = \frac{h_i' - \bar{h}_i^{\infty}}{RT^2} dT + \left(\frac{\bar{v}_i^{\infty}}{RT}\right) dP \tag{13}$$

where

h_i' = molar enthalpy of "i" in the ideal gas state

$\bar{h}_i^{\infty}$ = partial molar enthalpy of "i" at infinite dilution

$\bar{v}_i^{\infty}$ = partial molar volume of "i" at infinite dilution.

For experiments conducted at constant pressure, the second term in Equation (13) disappears. The expression for the temperature-dependency is then obtained by performing an indefinite integration on the remainder of the equation after assuming that the "enthalpy change of volatilization" $(h'_i - \bar{h}_i^{\infty})$ is constant with respect to temperature although this assumption is not entirely realistic with respect to some physical systems. The resulting equation is

$$\ln H_i = \frac{-(h_i' - \bar{h}_i^{\infty})}{RT} + C_1 \tag{14}$$

where

C_1 = integration constant.

Note that the integration must be done with the H_1 or H_1'' forms of Henry's law constant to account for changes in the bulk gas density with temperature.

By treating the quantities $(h'_i - \bar{h}^{\infty}_1)/R$ and C_1 as fitting parameters, H_1 data obtained at various temperatures can be correlated to Equation (14) using linear regression analysis. The final equation for H_i has the following form:

$$H_1'' = \text{EXP}\left(\frac{A}{T}\right) + B \qquad (15)$$

where A and B are the "best-fit" constants for the experimental data. All compounds are currently being tested at 5 °C increments from 10 °C to 30 °C, and a least-squares procedure on the resulting data is used to determine A and B. The interested reader should refer to Appendix B of this report for the temperature-regression plots generated during this study.

SECTION III

HENRY'S LAW CONSTANT MEASUREMENTS

Two techniques were used to measure Henry's law constant(s) for the compounds in this study. One was a batch air-stripping technique developed by Mackay et al. (Reference 5). The other was Equilibrium Partitioning in Closed Systems, a technique known as EPICS, originally proposed by Gossett and Lincoff (Reference 1). Each of these techniques will be described in the sections that follow, and the results of the measurements performed will be summarized.

A. BATCH AIR STRIPPING

The most common method for laboratory measurement of air-water partition coefficients for hydrophobic organics is batch air stripping, first proposed by Mackay et al. (Reference 5). Conceptually, the procedure is simple. High-purity air bubbled through a continuously mixed, organic-laden aqueous solution is allowed to equilibrate with the aqueous phase. This operation is typically carried out in a tall vertical column in which the gas is introduced at the bottom through a fine-pore frit. The combination of a tall column and a small bubble size (low bubble buoyancy) increase the degree to which gas-liquid equilibrium is approached. By monitoring the equilibrium gas (or liquid) concentration versus time, Henry's law constant can be determined with a high degree of precision.

1. Governing Theory

Henry's law constant is calculated by correlating concentration data against a solute mass-balance equation for the column. The differential form of the mass balance is written:

$$\text{IN} - \text{OUT} = \text{ACCUMULATION}$$

$$Y_o G - Y(t) G = \frac{d}{dt} \left(C(t) V\right) \tag{16}$$

where

Y_o = organic concentration at gas inlet, g moles/m^3

$Y(t)$ = time-variable outlet gas concentration, g moles/m^3

G = volumetric gas flow rate, m^3/minute

$C(t)$ = time-variable liquid concentration, g moles/m^3

V = total volume of batch liquid in column, m^3.

By substituting the Henry's law relationship $Y(t) = H_i C(t)$ into Equation (16) and integrating, the following expression results:

$$\ln C(t) = \ln C_o + \frac{H_i G}{V} \quad t \tag{17}$$

where

t = elapsed time from start of the run (minutes).

According to Equation (17), a logarithmic plot of liquid-phase (or gas phase) concentration data as a function of elapsed time will yield a straight line with a slope directly related to Henry's law constant. Linear regression analysis of the raw data is typically employed to determine the "best-fit" slope. It is not necessary to know the initial batch concentration, C_o, because only the y-intercept of the plot is influenced. The preparation of quantitative calibration standards to precisely determine absolute concentrations is not necessary for the same reason. Therefore, any proportional measure of liquid concentration, such as Ultraviolet (UV) absorbance in the water or gas chromatograph peak area from the air, can be inserted for C(t) in Equation (17). For the special case in which liquid sampling significantly affects the column volume, Equation (15) may be written for discrete sampling intervals:

$$\ln C_1 = \ln C_o + H_i G \sum \frac{\Delta t_i}{V_i} \tag{18}$$

where

C_i = liquid concentration at the end of the i^{th} time interval, gmoles/m^3

Δt_i = elapsed time on the i^{th} sampling period, in minutes

V_i = column liquid volume during the i^{th} sampling period, m^3.

This equation is appropriate for measurements of liquid samples periodically withdrawn from the column during operation.

2. Laboratory Procedures

A bubble-purge column was assembled from two glass, water-jacketed columns, each 2 feet long with a 1-inch inside diameter. The columns were joined with a Teflon® union and rubber o-ring seals. A glass-fritted disc with a 25 to 50-micron pore size was press-fitted into the column inlet. Air was supplied to the column from a tank of high purity compressed air with the flow rate controlled by a rotameter and integral needle valve. Purge air was sparged through a water-filled impinger before entering the bubble column to prevent water evaporation from the column. The column exit was fitted with a glass tee for exhausting column effluent to the fume hood and for sampling the exit gas by syringe from a gas-tight Teflon-faced septum. A constant flow of

temperature-controlled water was maintained through the column jacket to ensure isothermal operation over the entire liquid depth. Figure 1 shows a schematic of this system.

Before operation, the column was loaded with a known volume of distilled/deionized water. After the water reached the temperature of the water jacket, the liquid volume was increased to its ultimate value by pipetting a quantity of saturated organic solution into the column. The organic solution was introduced subsurface to minimize volatilization losses. The use of saturated stock solutions rather than neat organic, eliminates the difficulty of getting the organic into solution before starting a run. Gas flow was then initiated at the desired rate, and a few minutes were allowed for column flow patterns to stabilize before sampling was begun.

Samples of column effluent gas were collected with a gas-tight syringe and injected into a gas chromatograph with a flame ionization detector. The GC column consisted of a 14-inch by 1/8-inch O.D. stainless steel tube packed with 80/100 mesh Porasil® B. The advantage of using this column was that sample peak elution occurred within 30-45 seconds of injection, allowing real-time analysis of column exit gas concentrations.

For those compounds exhibiting fast decay of gas-phase concentration, the variation in time between sample collection and injection by syringe significantly degraded the test reproducibility and decay-curve linearity. For these compounds, the column exit gas was pumped through a 1/16-inch outer diameter stainless steel tube and passed through a 0.5 cc stainless steel sample loop attached to a six-port rotary valve. This valve was pneumatically activated to load the loop contents onto the GC column. Such an arrangement allowed almost instantaneous injection of sampled effluent gas.

3. Results and Discussion

Initial tests performed with the bubble purge column were aimed at optimizing the operating conditions and experimental procedures. Hexane was chosen as the first test compound because of its high Henry's law constant, as calculated from vapor pressure and solubility data. Hexane's high volatility would likely reveal any problems in reaching equilibrium with the chosen column design.

Tests were performed at a column temperature of 30 °C with the flow rate being varied between tests. The results of several tests performed using hexane solutions are shown in Table 2.

TABLE 2. BUBBLE PURGE TEST RESULTS--HEXANE

Air Flow Rate, cc/mm	Liquid Depth, cm	Hc, kPa-m3/mol
91.6	124	5.948
47.6	121	8.014
48.4	119	7.608
21.8	123	14.913
14.1	128	19.050

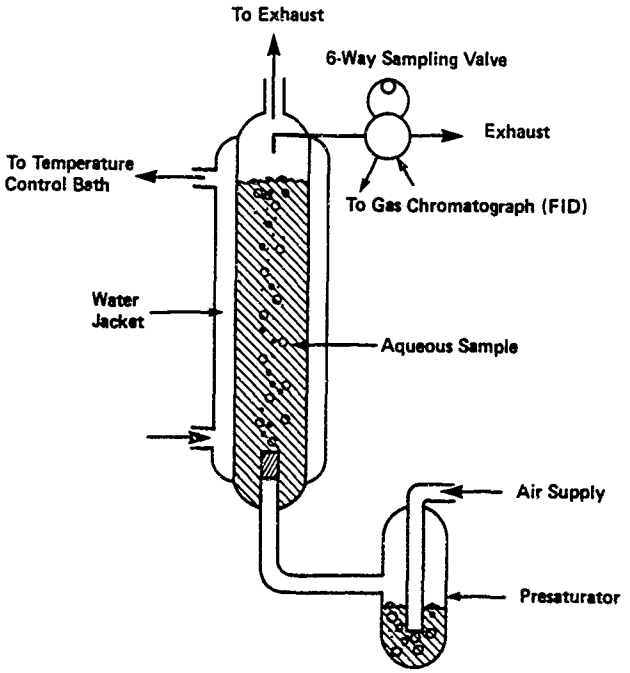

Figure 1. Schematic of Batch Air-Stripping Column.

At the lower gas flow rates, a smaller bubble size was produced and there appeared to be a corresponding improvement in the approach to equilibrium as evidenced by the increasing Henry's law constant. However, a subsequent test with only one section of the bubble purge column in place and a liquid depth of 56 cm produced a calculated Henry's law constant of 7.540 kPa-m^3/mole, nearly as high as the value observed at a depth of 119 cm with the same purge gas flow rate. If the changes observed in the Henry's law constant with changing gas flow rate were caused by equilibrium conditions not being met, one would expect a significant effect on the constant from decreasing the liquid depth by one-half.

Further tests were performed with 1,1,1-trichloroethane solutions. This compound has a much lower calculated constant than hexane and should have been much less susceptible to column equilibrium limitations. Tests were all performed at a column temperature of 30 °C with the liquid depth and gas flow rate being varied between tests. These results are shown in Table 3.

TABLE 3. BUBBLE-PURGE TEST RESULTS--1,1,1-TRICHLOROETHANE

Air Flow Rate, cc/min	Liquid Depth, cm	H, kPa-m^3/mol
24.8	54	2.258
27.2	120	3.636
27.3	122	3.508
104.0	54	2.212
106.0	75	2.474
106.0	100	2.756
108.0	120	2.870

Two observations can be made from these results. First, for a particular flow rate, increasing the liquid depth increased the Henry's law constant measured. Second, a variation in the measured Henry's law constant with changes in flow rate at a particular liquid depth was observed only for the two-section column (54 cm liquid depth tests were conducted with a single-column section). This second axial mixing within the column resulted in a bias in the measured decay rate, because such an effect would be more pronounced at lower flow rates and greater liquid depths.

To find column mixing efficiency, a test was performed to observe the dispersion of food coloring with the column liquid during operation. Water (about 575 mL) was added to the column to a depth of 115 cm and air flow was established at nominally 25 cc per minute. A few drops of red food coloring were added to the water at the top of the column and the dispersion was observed. Complete mixing was observed in the top column section within 2 minutes; however, approximately 25 minutes elapsed before the bottom column section reached the same color intensity.

Two steps were taken to prevent axial mixing problems from biasing the results for the remaining measurements using batch air stripping. First, only the lower 2-foot column section was used because of the considerable

problems observed in mixing between column sections. Second, all measurements were performed with a minimum air purge rate of 60 cc per minute. Henry's law constants were measured using this technique at temperatures of 10 °C, 15 °C, 20 °C, 25 °C, and 30 °C for 1,1,1-trichloroethane, cyclohexane, n-hexane, and 2-methylpentane. Each test was performed at two different liquid depths to provide some measure of satisfying equilibrium conditions. The results are shown in Tables 4 through 7, with the Henry's law constant shown as a mean and standard deviation (with the coefficient of variation) where multiple tests for the same conditions were performed. Additional batch air-stripping results for methyl ethylbenzene, p-xylene, benzene, mesitylene, 1,1,1-trichloroethane, and 1,2-dichloroethane were obtained at 25 °C to act as spot checks on the EPICS data.

TABLE 4. BATCH AIR STRIPPING RESULTS--1,1,1-TRICHLOROETHANE

Temperature, °C	Liquid depth, cm	H, kPa-m^3/mol
10	54.0	0.946 ± 0.037 (4.0)
10	57.5	1.020 ± 0.007 (0.7)
15	54.0	1.276 ± 0.012 (0.94)
15	57.5	1.303 ± 0.014 (1.1)
20	54.0	1.478 ± 0.026 (1.8)
25	57.5	1.553 ± 0.003 (0.2)
25	57.5	1.783 ± 0.028 (1.6)
30	54.0	2.204 ± 0.011 (0.5)

TABLE 5. BATCH AIR-STRIPPING RESULTS--CYCLOHEXANE

Temperature, °C	Liquid depth, cm	H, kPa-m^3/mol
10	54.0	3.498 ± 0.158 (4.5)
10	57.5	3.496 ± 0.047 (1.4)
15	54.0	3.668 ± 0.012 (0.3)
15	57.5	3.784 ± 0.066 (1.7)
20	54.0	4.614 ± NA
20	57.5	4.550 ± NA
25	54.0	5.222 ± NA
25	57.5	5.128 ± NA
30	54.0	5.807 ± 0.072 (1.2)
30	57.5	5.531 ± 0.332 (6.0)

TABLE 6. BATCH AIR-STRIPPING RESULTS--HEXANE

Temperature, °C	Liquid depth, cm	H, kPa-m^3/mol
10	54.0	4 468 ± 0.054 (1.2)
10	57.5	4.074 ± 0.016 (0.4)
15	54.0	4.700 ± 0.141 (3.0)
15	57.5	4.780 ± 0.303 (6.3)
20	54.0	5.265 ± NA
20	57.5	5.168 ± 0.026 (0.5)
25	54.0	5.391 ± 0.032 (0.6)
25	57.5	5.397 ± 0.167 (3.1)
30	54.0	5 957 ± 0.038 (0.6)
30	57.5	5.973 ± NA

TABLE 7. BATCH AIR STRIPPING RESULTS--METHYL PENTANE

Temperature, °C	Liquid depth, cm	H, kPa-m^3/mol
10	54.0	4.322 ± 0.134 (3.1)
10	57.5	4.282 ± 0.076 (1.8)
15	54.0	4.618 ± 0.098 (2.1)
15	57.5	4 740 ± 0.040 (0.85)
20	54.0	5.018 ± 0.052 (1.0)
20	57.5	5.010 ± 0.099 (2.0)
25	54.0	5.322 ± 0.014 (0.27)
25	57.5	5.292 ± 0.176 (3.3)
30	54.0	5.990 ± 0.004 (0.06)
30	57.5	5.956 ± 0.009 (0.15)

B. EQUILIBRIUM PARTITIONING IN CLOSED SYSTEMS (EPICS)

1. Governing Theory

Because of the equilibrium limitations of the batch air-stripping technique, the EPICS method is an attractive alternative for determining Henry's law constant. The EPICS procedure (Reference 1) is based on a closed system mass balance for a given VOC distributed between liquid and gas phases in contact. A component balance takes the general form:

$$M = C_L V_L + C_G V_G \qquad (19)$$

where

M = total organic mass in the system

C_L = liquid-phase organic concentration

C_G = gas-phase organic concentration

V_L = total liquid volume

V_G = total gas volume

If the same mass of organic is introduced into two closed containers (i.e., sealed septum bottles) containing different volumes of pure water, an expression similar to Equation (19) may be written for each system. Equating these mass balance expressions and introducing Henry's law to substitute for the liquid-phase VOC concentrations gives an equation relating Henry's constant to headspace concentrations and known volumes:

$$H' = \frac{(C_{G_1}/C_{G_2})V_{L_1} - V_{L_2}}{V_{G_2} - (C_{G_1}/C_{G_2})V_{G_1}} \qquad (20)$$

where

H' = dimensionless Henry's law constant, atm • (m^3 of liquid)/(m^3 of gas)

1,2 = subscripts identifying the two closed systems.

The only experimental information needed to determine Henry's law constant is the ratio of gas-phase concentrations (C_{G_1}/C_{G_2}) in the two systems. In fact, absolute concentrations are not necessary because any proportional measure of concentration (such as GC peak areas) will yield the desired headspace ratio in Equation (20).

2. Laboratory Procedures

In practice, the EPICS method involves measurement of multiple pairs of high/low volume closed systems to obtain several independent estimates of Henry's law constant. If three pairs are used, for example, three replicate headspace measurements will be obtained for each of the two liquid volumes. Thus, the six values can be paired in all permutations to calculate nine estimates of Henry's law constant. Typically, an arithmetic average of these estimates is taken to be the true Henry's law constant, with the coefficient of variation for the individual values reported.

The EPICS technique used during the current VLE program uses two replicate bottle pairs per observation to obtain four estimates of Henry's constant, and a second set of selected compounds is analyzed on a separate day to determine day-to-day precision. Therefore, a total of eight Henry's law constant estimates are obtained for a selected component.

A saturated stock solution for each component is prepared by adding an amount of organic solute slightly in excess of the solubility limit to a volume of pure deionized/distilled water. All organic chemicals were used at

least 99 percent purity. All stock solutions are prepared in 1-liter amber bottles and allowed to equilibrate for a minimum of 1 week before use. For compounds more dense than water, solution is withdrawn directly from the amber bottles to prepare EPICS samples. For compounds less dense than water, the stock solution is transferred to a 500 mL separatory funnel the day before the scheduled EPICS tests, then withdrawn the next day from the bottom of the separatory funnel to prepare the EPICS sample bottles.

In preparing EPICS samples, four 250 mL amber glass bottles are filled with 20 mL and 200 mL, respectively, of deionized/distilled water into two bottles. The same volume of saturated stock solution is then added to each of the four septum bottles. The exact solution volume added is dependent upon compound solubility and each test was chosen to produce an initial liquid concentration of 10 mg per liter in the 200 mL system. For high concentration stock solutions, 1 cc was chosen as the lower limit for addition to the EPICS bottles. For low concentration stock solutions, 10 cc was chosen as the upper limit to be added.

In addition to the EPICS samples, one extra bottle per compound is prepared for use in testing and conditioning the GC system. Also, one blank bottle consisting of deionized/distilled water only, is prepared for every 10 EPICS sample bottles prepared. The bottles are sealed with a silicone rubber spectrum cap with a Teflon® liner facing toward the bottle headspace. These liners are used only once to prevent adsorption of test compound into the silicone rubber once the liner has been pierced. The loaded bottles are shaken vigorously by hand and then completely submersed in a constant temperature water bath for a minimum of 16 hours before analysis. This period was determined to be adequate to attain a constant (equilibrium) headspace concentration with respect to time for all of the chemicals examined.

After equilibration, headspace samples are withdrawn from the bottles via Hamilton 1.0 cc gas-tight syringe and injected into a Varian 3700 gas chromatograph equipped with a flame ionization detector (FID). The GC column is identical to that used for batch air-stripping tests. Component retention times are typically less than 1 minute.

To check detector response linearity and the validity of Henry's law over the concentration range used, a series of quantitative standards is prepared and analyzed for each component. The standard series consists of varying volumes of saturated stock solution diluted to the same volume with deionized/distilled water in 250 mL septum bottles. Response linearity is checked by plotting headspace gas chromatograph (GC) response versus volume of saturated stock solution. The results of all of these tests are shown in Appendix B.

3. Results

Measurement of Henry's law constant using EPICS has been performed for 48 of the 51 compounds proposed. The headspace concentrations produced by samples of anthracene, bis (2-ethylhexyl) phthalate, and 1,2-dinitrotoluene were below the limit of detection of the GC-FID. This was expected, based on

the extremely low solubility (and thus, low stock solution concentration) of these compounds as well as low vapor pressure. Unfortunately, liquid-phase measurements for these materials were also inadequate, because virtually no organic partitions into the headspace, and the measurements cannot be distinguished from the dilution factors. For the remaining compounds, four constants were determined for each compound at temperatures of 10, 15, 20, 25, and 30 °C. These results are summarized in Table 8 in terms of the temperature regression study and are presented in detail in Appendix B.

Measurements of Henry's law constant have been repeated for these compounds that exhibited poor correlation coefficients for the linear regression of H_1 (Henry's law constant) versus reciprocal absolute temperature. In the repeat measurements, EPICS bottles were immersed in the water bath to their necks during equilibration. This was made possible by preparing fewer bottles and using metal clips to prevent low liquid volume bottles from floating.

A major objective of this investigation was to reduce the Henry's law constant data to a final form useful for manual or computer calculations. The chosen means to accomplish this was to generate temperature regression equations based on the theoretical constant-pressure temperature dependence of Henry's law constant. The expression describing this dependence was presented earlier as Equation (15). The "enthalpy of volatilization" is assumed constant over the entire temperature range in the regression, even though such a simplification may not always be physically realistic. Generally, the simple two-constant fit seemed to represent the data well, as evidenced by typical r-squared values in excess of 0.95. Given the rigorous statistics calculated for the data over the course of the study, attaching reliable error bounds to the regression equation proved possible. Table 8, therefore, completely describes the data as a temperature regression equation coupled with a temperature-dependent error term, with upper and lower error limits in absolute units (Henry's law constant units) or as upper and lower percentage limits. Of the original 51 chemicals, the results for 48 are presented in Table 8.

An examination of Table 8 reveals very good r-squared values for the linear temperature regression for most of the chemicals examined; however, such results have not been achieved for a few compounds. Using an r-squared value of 0.95 as a somewhat arbitrary cutoff point for assessing the quality of it, the initial temperature regression fits for 21 of the 51 chemicals of interest were deemed to be inadequate. The entire EPICS series was repeated for these 21 chemicals. Careful replication of these compounds in some cases yielded correlations of improved quality. This can be taken as an indication that the EPICS technique itself is not the cause of the poor temperature regression correlation noted for a few of the chemicals investigated, but that either a linear regression equation does not appropriately describe the thermodynamics for that mixture, or the Henry's law constant is outside the range appropriate to headspace measurements. Improvement for some of the compounds can be attributed to the refinement of the EPICS technique over the project's course. Table 9 shows the 95 percent confidence bands for the 48 chemicals 25° C calculated from the equations presented in Table 8.

TABLE 8. COMPONENT PARAMETERS FOR THE TEMPERATURE REGRESSION EQUATION AND ITS ASSOCIATED 95 PERCENT CONFIDENCE ERROR TERM

Number	Component name	Temperature regression parameters[a]			Error term parameters[b]		
		Slope, A	Y-Int., B	r^2	x-Mean, $\bar{x}$	S_{xx}	"s"
1	Nonane	-5.4975E+03	1 1304E+01	0.6165	3 4132E-03	3.3933E-08	2 9341E-01
		-2.0208E+02	-1.8469E-01	0.0128	3.4096E-03	3.0100E-08	1.7790E-01
2	Hexane	-7.5300E+03	2 5256E+01	0.9173	3 4132E-03	3.3933E-08	2 4042E-01
3	2-Methylpentane	-9.5723E+02	2.9590E+00	0.4974	3.4132E-03	3.3933E-08	1.0234E-01
		-7.4681E+03	2.4943E+01	0.3205	3 4095E-03	3.0030E-08	1 0880E+00
4	Cyclohexane	-3.2376E+03	9 1407E+00	0.9815	3.4132E-03	3 3933E-08	4.7322E-02
5	1,2-Dichlorobenzene	-1 4222E+03	-1.5188E+00	0 4641	3.4130E-03	3.9338E-08	1.6253E-01
		-3.6351E+03	6.0146E+00	0 7784	3.4120E-03	3.2370E-08	2 0147E-01
6	Chlorobenzene	-2.6894E+03	3 4687E+00	0 9646	3.4130E-03	3.3938E-08	5 4787E-02
7	1,3-Dichlorobenzene	-2.5638E+03	2.8920E+00	0.8501	3.4130E-03	3.3938E-08	1.1451E-01
		-4.4853E+03	9.2298E+00	0.8196	3.4120E-03	3.2370E-08	2.1760E-01
8	1,4-Dichlorobenzene	-2.7198E+03	3 3726E+00	0.9411	3.4130E-03	3.3938E-08	7.2363E-02
		-3.6364E+03	6 4179E+00	0.9671	3.4120E-03	3.2370E-08	6.9724E-02
9	o-Xylene	-3.2196E+03	5.5410E+00	0 9659	3.4127E-03	3 3946E-08	6.4381E-02
10	p-Xylene	-3.5200E+03	6.9307E+00	0.9889	3.4127E-03	3 3946E-08	3.9582E-02
11	m-Xylene	-3.3372E+03	6.2799E+00	0.9978	3.4127E-03	3.3946E-08	1.6858E-02
12	Propylbenzene	-3.6814E+03	7.8350E+00	0.9968	3.4127E-03	3 3946E-08	2.2348E-02
13	Ethylbenzene	-3.2410E+03	6.1047E+00	0.9335	3.4127E-03	3.3946E-08	9 2000E-02
		-4.9941E+03	1.1916E+01	0.9994	3 4126E-03	3.3861E-08	1 2664E-02
14	Toluene	-3.0242E+03	5.1331E+00	0.9828	3 4132E-03	3.4078E-08	4 2640E-02
15	Benzene	-3.1942E+03	5.5340E+00	0.9877	3.4132E-03	3.3933E-08	6.2070E-02
16	Phenol	-4.6588E+03	1.1320E+01	0 9840	3.4132E-03	3.4078E-08	6.3276E-02
17	Methyl ethylbenzene	-3.1792E+03	5.5566E+00	0.9682	3 4132E-03	3.4078E-08	6.1392E-02
18	1,1-Dichloroethane	-3.1369E+03	5.4842E+00	0.9930	3.4132E-03	3 3567E-08	2.7933E-02
19	1,2-Dichloroethane	-1.5223E+03	-1.3714E+00	0 8777	3.4130E-03	3.3699E-08	6.0221E-02
		-4.6198E+03	6.9421E+00	0.9911	3.4130E-03	3 3638E-08	4.0235E-02
20	1,1,1-Trichloroethane	-3 3987E+03	7 3585E+00	0 9983	3.4127E-03	3.3832E-08	1.5050E-02
21	1,1,2-Trichloroethane	-3.4320E+02	-5.6128E+00	0.1043	3.4127E-03	3.3946E-08	1.0701E-01
		-4.8432E+03	9.3261E+00	0.9683	3 4130E-03	3.3638E-08	9 2850E-02
22	cis-Dichloroethylene	-3.1478E+03	5.1637E+00	0.9735	3.4134E-03	3.3987E-08	6.5243E-02
23	trans-Dichloroethylene	-2.9638E+03	5.3330E+00	0.9854	3.4134E-03	3.3987E-08	3.8364E-02
24	Tetrachloroethylene	-4.3679E+03	1 0646E+01	0.9872	3 4134E-03	3.3987E-08	5.2903E-02
25	Trichloroethylene	-3.7018E+03	7.8445E+00	0.9984	3.4134E-03	3.3987E-08	1.5539E-02
26	Naphthalene	1.5976E+03	-1.2515E+01	0.0339	3.4130E-03	3.4086E-08	9 0978E-01
27	Tetralin	7.6177E+02	-8 7330E+00	0.0580	3.4130E-03	3.4086E-08	3.2722E-01
		-5.3918E+03	1.1029E+01	0.9955	3.4130E-03	3.3638E-08	3.8394E-02
28	Decalin	-4.1250E+03	1.1848E+01	0 9192	3.4130E-03	3.4086E-08	1.3037E-01
		-5.1728E+03	1.5428E+01	0.9343	3.4126E-03	3.3861E-08	1 4669E-01
29	Anthracene	--	--	--	--	--	--
30	Vinyl chlorine	-2.7176E+03	5.0781E+00	0.7608	3.4127E-03	3.3946E-08	1.6208E-01
		-2.9369E+03	6.1383E+00	0.9700	3.4128E-03	3.4072E-08	5.4972E-02
31	Chloroethane	-2.5881E+03	4.2649E+00	0.9835	3.4127E-03	3.3946E-08	3.5575E-02
32	Hexachloroethane	-2.5504E+03	3.7435E+00	0.7682	3.4127E-03	3.3948E-08	1 4903E-01
		-5.6273E+03	1.4103E+01	0.6876	3.4126E-03	3.3861E-08	4.0301E-01

(continued)

TABLE 8. COMPONENT PARAMETERS FOR THE TEMPERATURE REGRESSION EQUATION AND ITS ASSOCIATED 95 PERCENT CONFIDENCE ERROR TERM (concluded)

Number	Component name	Temperature regression parameters[a]			Error term parameters[b]		
		Slope, A	Y-Int., B	r^2	x-Mean, $\bar{x}$	S_{xx}	"s"
33	Carbon tetrachloride	-3.9514E+03	9.7393E+00	0.9965	3.4127E-03	3.3946E-08	2.4766E-02
34	1,3,5-Trimethylbenzene	-3.6277E+03	7.2408E+00	0.9622	3.4132E-03	3.4078E-08	7.6628E-02
35	bis(2-Ethylhexyl) phthalate	--	--	--	--	--	--
36	Ethylene dibromide	1.9610E+03	-1.3978E+01	0.2208	3.4132E-03	3.3933E-08	3.9178E-01
		-3.8764E+03	5.7031E+00	0.9281	3.4128E-03	3.4072E-08	1.1502E-01
37	1,1-Dichloroethylene	-2.9074E+03	6.1228E+00	0.9735	3.4132E-03	3.3933E-08	5.1054E-02
38	Methylene chloride	-4.2682E+03	8.4828E+00	0.9878	3.4127E-03	3.3347E-08	4.9998E-02
		-4.0653E+03	7.8540E+00	0.9050	3.4129E-03	3.3344E-08	1.3883E-01
39	Chloroform	-5.0300E+03	1.1408E+01	0.0974	3.4132E-03	3.3933E-08	2.7491E-02
		-4.1192E+03	8.4651E+00	0.9988	3.4129E-03	3.3344E-08	1.4911E-02
40	1,1,2,2-Tetrachloroethane	-2.8099E+03	1.7257E+00	0.1940	3.4126E-03	3.4919E-08	6.1801E-01
41	1,2-Dichloropropane	-4.7079E+03	9.8428E+00	0.8203	3.4133E-03	3.4024E-08	2.3468E-01
42	Dibromochloromethane	-6.3731E+03	1.4617E+01	0.9136	3.4133E-03	3.4024E-08	2.0869E-01
43	1,2,4-Trichlorobenzene	-4.0280E+03	7.3605E+00	0.8188	3.4106E-03	3.2195E-08	1.9628E-01
44	2,4-Dimethylphenol	3.3072E+03	-1.6336E+01	0.5552	3.4106E-03	3.2195E-08	3.0664E-01
45	1,1,2-Trichlorotrifluoroethane	-3.2429E+03	9.6487E+00	0.9318	3.4129E-03	3.3344E-08	9.2470E-02
46	Methyl ethyl ketone (MEK)	-2.3139E+03	-4.8370E-01	0.8229	3.4137E-03	3.3605E-08	1.1343E-01
		5.2141E+03	-2.6322E+01	0.7973	3.4108E-03	3.2617E-08	2.7412E-01
47	Methyl isobutyl ketone (MIBK)	-1.6060E+02	-7.1569E+00	0.0015	3.4137E-03	3.3605E-08	4.3627E-01
		-1.7851E+03	-2.8235E+00	0.4058	3.4110E-03	3.2613E-08	2.2524E-01
48	Methyl cellosolve	8.7376E+02	-6.0502E+00	0.0233	3.4137E-03	3.3605E-08	5.9828E-01
49	bis(2-Chloroethyl) ether	1.5703E+04	-6.2146E+01	0.6716	3.4118E-03	3.3778E-08	1.1652E+00
50	Trichlorofluoromethane	-3.5132E+03	9.4799E+00	0.9975	3.4118E-03	3.3778E-08	1.8678E-02
51	2,6-Dinitrotoluene	--	--	--	--	--	--

[a]Temperature regression equation: $\ln H = \frac{A}{T} + B$; H in (atm-m^3/mol); T in (K).

[b]95 percent confidence error term: $E_{lower}(\%) = (e^{-Y} - 1) \times 100$; $E_{upper}(\%) = (e^{Y} - 1) \times 100$; $Y = (t)(s)\sqrt{\frac{1}{n} + \frac{\left(\frac{1}{T} - \bar{x}\right)^2}{S_{xx}}}$.

n = 5 (number of data points in regression), t = 3.182 (t-value for n-2 degrees of freedom); s = estimate of the standard deviation. Confidence limits: $H_{95\%} = \text{EXP}\ \frac{A}{T} + B \pm Y$. $H_{95\%}$ in (atm-m^3/mol), T in (K).

[c]Components 29, 35, and 51 (anthracene, bis(2-ethylhexyl)phthalate, and 2,6 dinitrotoluene, respectively) are omitted from the table because of detection limit problems.

TABLE 9. TEMPERATURE REGRESSION PARAMETERS AND ERROR BANDS (AT 25 °C) FOR 51 ORGANIC CHEMICALS

Number	Component name	Temperature regression fit[a]			95% Confidence band (25 °C)	
		Slope, A	Y-Int , B	r^2	Lower, %	Upper, %
1	Nonane	-3.4975E+03	1.1304E+01	0.6165	-40.20	67.22
		-2.0208E+02	-1.8469E-01	0.0128	-26.76	36.54
2	Hexane	-7.5366E+03	2.5260E+01	0.9173	-34.38	62.39
3	2-Methylpentane	-9.5723E+02	2.9590E+00	0.4974	-16.42	19.64
		-7.4881E+03	2.4943E+01	0.3205	-85.11	571.39
4	Cyclohexane	-3.2376E+03	9.1407E+00	0.9815	-7.96	8.65
5	1,2-Dichlorobenzene	-1.4222E+03	-1.5180E+00	0.4641	-24.76	32.90
		-3.6351E+03	6.0146E+00	0.7784	-29.76	42.30
6	Chlorobenzene	-2.6894E+03	3.4687E+00	0.9648	-9.14	10.06
7	1,3-Dichlorobenzene	-2.5638E+03	2.8820E+00	0.8501	-18.16	22.19
		-4.4653E+03	9.2298E+00	0.8196	-31.72	46.46
8	1,4-Dichlorobenzene	-2.7198E+03	3.3726E+00	0.9411	-11.89	13.50
		-3.6364E+03	6.4179E+00	0.9671	-11.51	13.01
9	o-Xylene	-3.2196E+03	5.5410E+00	0.9659	-10.64	11.91
10	p-Xylene	-3.5200E+03	6.9307E+00	0.9889	-6.68	7.16
11	m-Xylene	-3.3372E+03	6.2799E+00	0.9978	-2.90	2.99
12	Propylbenzene	-3.6814E+03	7.8350E+00	0.9968	-3.83	3.98
13	Ethylbenzene	-3.2410E+03	6.1647E+00	0.9335	-14.85	17.44
		-4.9941E+03	1.1915E+01	0.9994	-2.19	2.24
14	Toluene	-3.0242E+03	5.1331E+00	0.9828	-7.19	7.75
15	Benzene	-3.1942E+03	5.5340E+00	0.9677	-10.31	11.49
16	Phenol	-4.6580E+03	1.1320E+01	0.9840	-10.49	11.72
17	Methyl ethylbenzene	-3.1792E+03	5.5566E+00	0.9682	-10.19	11.35
18	1,1-Dichloroethane	-3.1369E+03	5.4842E+00	0.9930	-4.78	5.03
19	1,2-Dichloroethane	-1.5223E+03	-1.3714E+00	0.8777	-10.01	11.13
		-4.0198E+03	8.9421E+00	0.9911	-6.81	7.31
20	1,1,1-Trichloroethane	-3.3987E+03	7.3505E+00	0.9983	-2.60	2.67
21	1,1,2-Trichloroethane	-3.4320E+02	-5.6128E+00	0.1043	-17.06	20.56
		-4.8432E+03	9.3201E+00	0.9683	-15.02	17.67
22	cis-Dichloroethylene	-3.1428E+03	5.1537E+00	0.9735	-9.24	10.18
23	trans-Dichloroethylene	-2.9838E+03	5.3330E+00	0.9854	-6.51	6.97
24	Tetrachloroethylene	-4.3679E+03	1.0646E+01	0.9872	-8.86	9.72
25	Trichloroethylene	-3.7018E+03	7.8445E+00	0.9984	-2.69	2.76
26	Naphthalene	1.5976E+03	-1.2515E+01	0.0339	-79.63	390.83
27	Tetralin	7.6177E+02	-8.7330E+00	0.0580	-43.57	77.22
		-5.3918E+03	1.1829E+01	0.9955	-6.51	6.96
28	Decalin	-4.1250E+03	1.1848E+01	0.9192	-20.39	25.61
		-5.1728E+03	1.5428E+01	0.9343	-22.47	28.98
29	Anthracene	--	--	--	--	--
30	Vinyl chloride	-2.7176E+03	5.0781E+00	0.7608	-24.67	32.74
		-2.9309E+03	6.1383E+00	0.9700	-9.15	10.08
31	Chloroethane	-2.5801E+03	4.2649E+00	0.9836	-6.03	6.41
32	Hexachloroethane	-2.5504E+03	3.7435E+00	0.7682	-22.93	29.75
		-5.6273E+03	1.4103E+01	0.6876	-50.54	102.26

(continued)

TABLE 9. TEMPERATURE REGRESSION PARAMETERS AND ERROR BANDS (AT 25 °C) FOR 51 ORGANIC CHEMICALS (concluded)

Number	Component name	Temperature regression fit[a]			95% Confidence band (25 °C)	
		Slope, A	Y-Int., B	r^2	Lower, %	Upper, %
33	Carbon tetrachloride	-3.9514E+03	9.7393E+00	0.9965	-4.23	4.42
34	1,3,5-Trimethylbenzene	-3.8277E+03	7.2408E+00	0.9622	-12.56	14.36
35	bis(2-Ethylhexyl) phthalate	--	--	--	--	--
36	Ethylene dibromide	1.9810E+03	-1.3978E+01	0.2208	-49.67	98 68
		-3.8764E+03	5.7031E+00	0 9281	-10 20	22 25
37	1,1-Dichloroethylene	-2.9074E+03	6.1228E+00	0.9736	-8.56	9.36
38	Methylene chloride	-4.2682E+03	8.4828E+00	0.9878	-8.39	9.16
		-4.0653E+03	7.8540E+00	0.9050	-21.62	27.59
39	Chloroform	-5.0360E+03	1.1408E+01	0.9974	-4.70	4.94
		-4.1192E+03	8.4651E+00	0.9988	-2.58	2.65
40	1,1,2,2-Tetrachloroethane	-2.8099E+03	1.7267E+00	0.1940	-85.83	192.67
41	1,2-Dichloropropane	-4.7079E+03	9.8428E+00	0.8203	-33.72	50.88
42	Dibromochloromethane	-6.3731E+03	1.4617E+01	0.9136	-30.83	44 16
43	1,2,4-Trichlorobenzene	-4.0288E+03	7.3605E+00	0.8188	-28.94	40.73
44	2,4-Dimethylphenol	3.3072E+03	-1.6336E+01	0.5552	-41.36	70.54
45	1,1,2-Trichlorotrifluoroethane	-3.2429E+03	9.6487E+00	0.9318	-14.98	17.62
46	Methyl ethyl ketone (MEK)	-2.3139E+03	-4.8370E+01	0 8229	-16.10	22.10
		5.2141E+03	-2.6322E+01	0.7973	-37.93	61 10
47	Methyl isobutyl ketone (MIBK)	-1.0860E+02	-7.1589E+00	0.0015	-53.61	115 57
		-1.7851E+03	-2.8235E+00	0.4058	-32 45	48 05
48	Methyl cellosolve	8.7376E+02	-6 0502E+00	0.0233	-65.12	186.88
49	bis(2-Chloroethyl) ether	1.5703E+04	-6.2146E+01	0.6716	-86 83	659.06
50	Trichlorofluoromethane	-3.5132E+03	9.4799E+00	0.9975	-3.20	3.30
51	2,6-Dinitrotoluene	--	--	--	--	--

[a] $\ln H = \frac{A}{T} + B$; T in K, H in (atm-m^3/mol).

[b] 95 percent confidence limits at 25 °C for the temperature regression line.

In some cases, the linear correlation of the logarithm of the Henry's law constant and temperature as described by Equation (13) results in an exceedingly poor correlation coefficient, even for replicated compounds. For example, in Figure 2 the temperature regression plot for 2-methyl pentane (Component 103) is shown. For this compound a linear regression may not be appropriate, but clearly the data could be represented by a smooth curve with a local minimum near 20 °C.

The Henry's law constant may be defined in terms of the infinite dilution activity coefficient and the pure-component vapor pressure (Equation 7). Many solutions, particularly aromatics in water, are known to have an activity coefficient maximum in the range of 10-25 °C (Tsonopaulos and Praunsnitz, Reference 6). This being the case, it is not surprising that those materials with a strong activity coefficient dependence on temperature, might also show a strongly nonlinear Henry's law constant behavior. As shown in Section III on the solubility measurements, minima and maxima in solubility are indeed noted with increasing temperature. A theoretically sound correlation of activity coefficients, taking into account the structure of water as a function of temperature, has not yet been proposed to explain this phenomenon.

A second and probably more important measure of data quality is the coefficient of variation (COV) for individual data sets, particularly for replicates at one temperature. However, poor temperature regressions generally correspond to high COV values for the EPICS four-bottle series at all temperatures. Figures 3 through 7 present the COV values for the compounds with a good linear regression correlation plotted against their respective Henry's law constants at each of the five target temperatures (10, 15, 20, 25, and 30 °C). Table 10 summarizes all of the COV values. The only discernable trend apparent in these plots is a general rise in the COV value with decreasing volatility, an effect that may be due to reduced sensitivity of the analytical instrumentation. An examination of the average COV values in Figures 3 through 7 indicates an overall EPICS four-bottle precision of 5 percent or better over the whole volatility range.

Finally, the actual Henry's law constants, as measured at each of the temperatures for all of the chemicals, are listed in Table 11. The expanded raw data including all of the statistical data are listed in Appendix B.

4. Evaluation of the Results

A comparison of selected results of this study and results of previous studies is found in Table 12. Comparisons of Henry's law constants from EPICS in this study to bubble column results are quite good with three exceptions. A difference of over 69 percent is observed for cyclohexane and can be attributed to the failure to attain equilibrium in the bubble column tests.

As expected, the greatest difference between the results of this study and other reported values occurs in the comparison with Henry's Law constants predicted from vapor pressure and solubility data. The differences, both positive and negative, ranged from 2 to 400 percent, with no distinct pattern attributable to chemical type or structure. However, it is not uncommon for

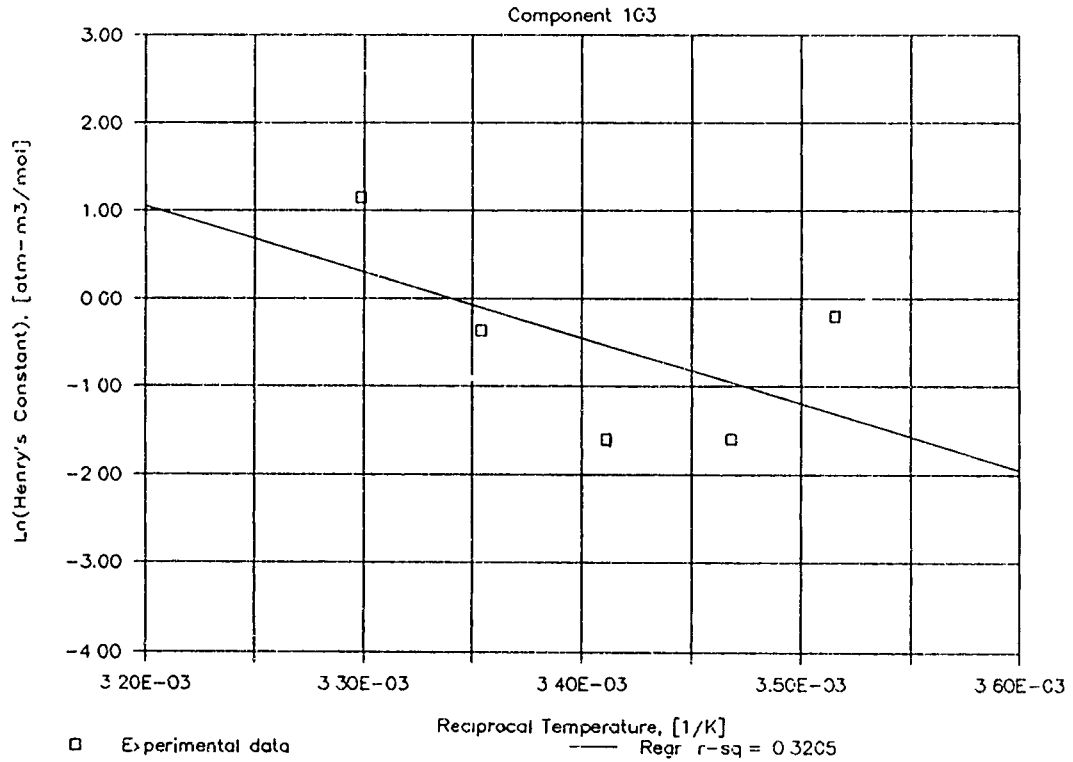

Figure 2. Temperature Regression Plot for 2-Methyl Pentane.

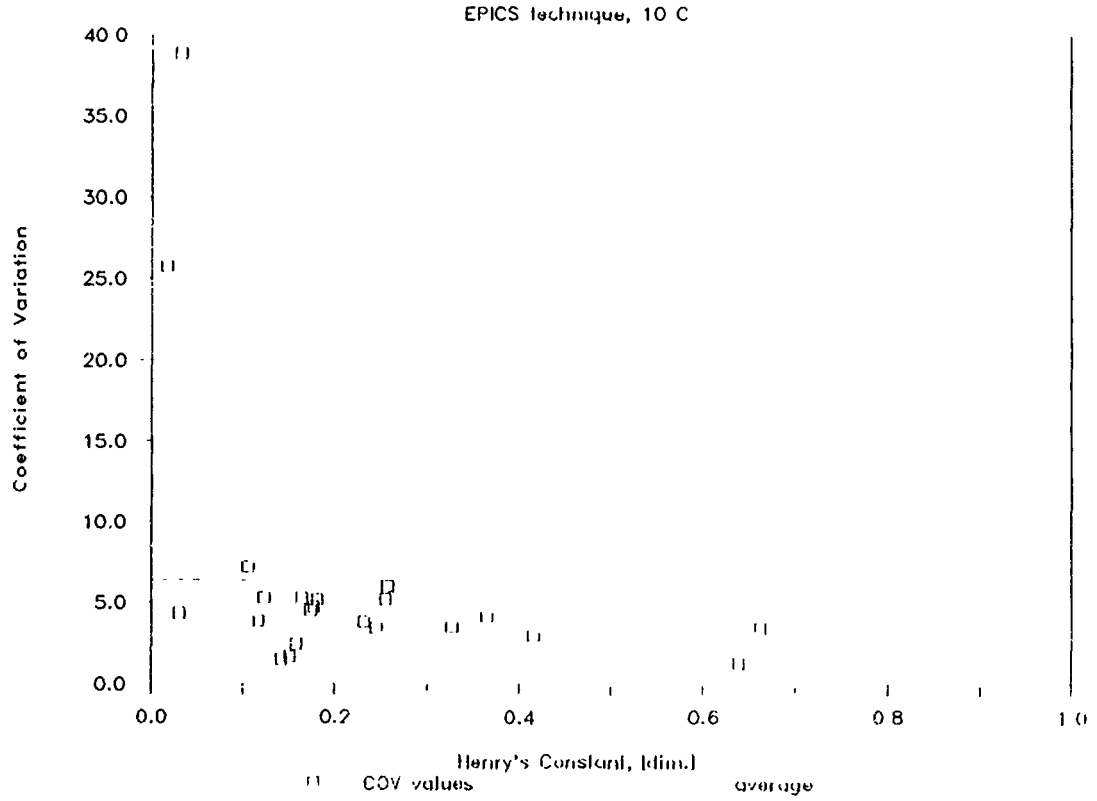

Figure 3. Coefficient of Variance Values vs. Henry's Constant for the EPICS at 10 °C.

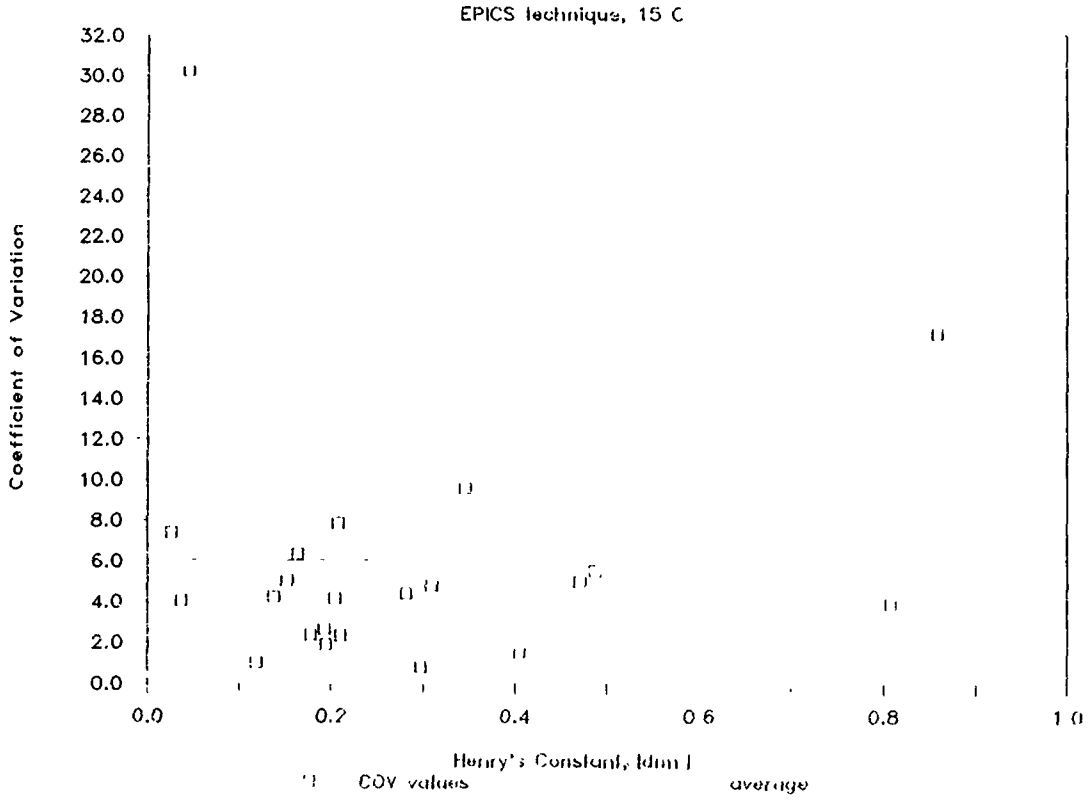

Figure 4. Coefficient of Variance Values vs. Henry's Constant for the EPICS at 15 °C.

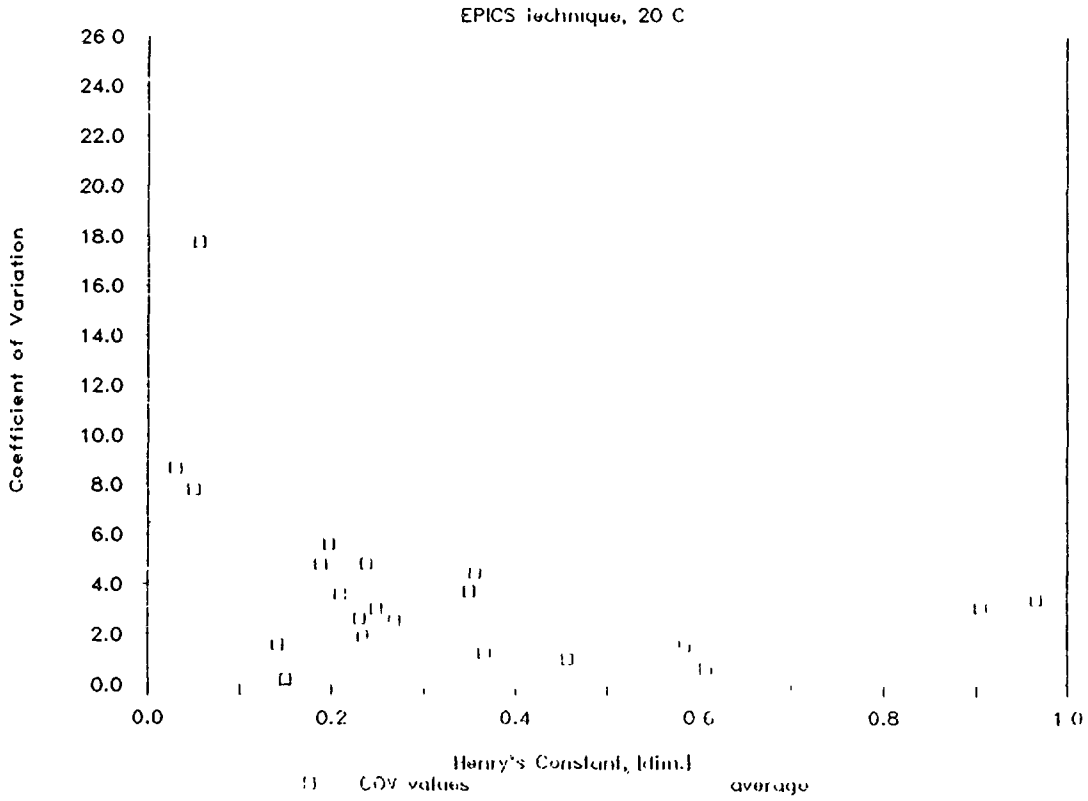

Figure 5. Coefficient of Variance Values vs. Henry's Constant for the EPICS at 20 °C.

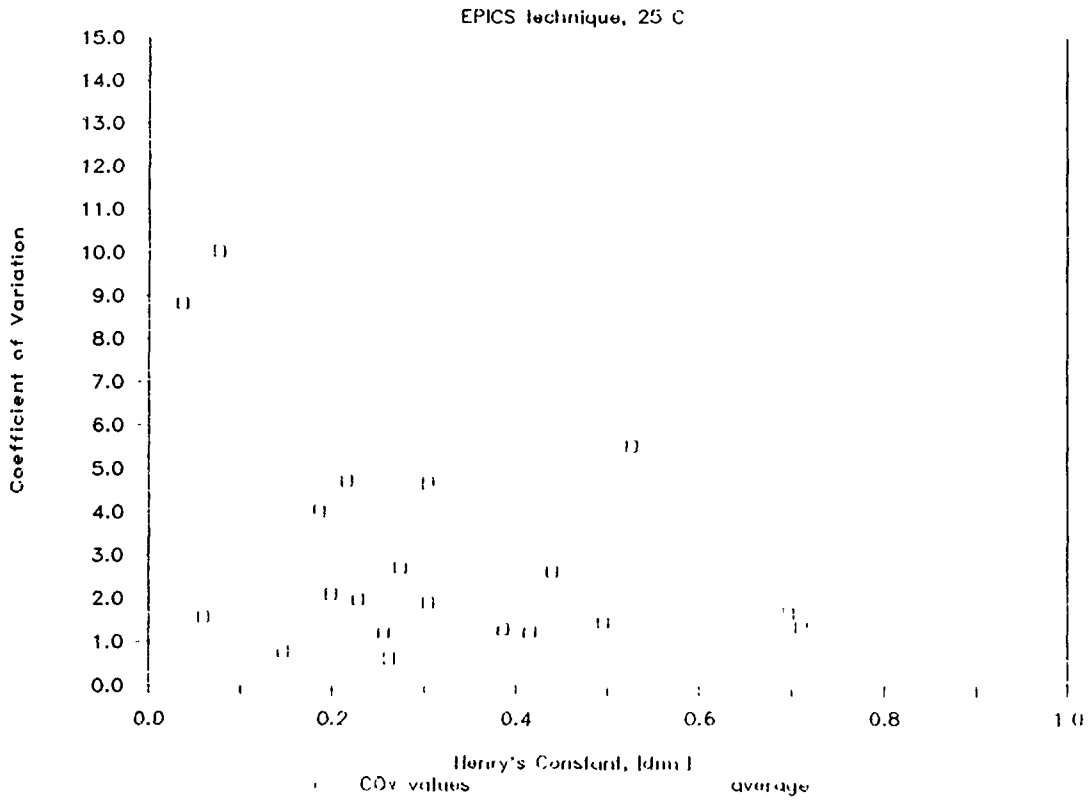

Figure 6. Coefficient of Variance Values vs Henry's Constant for the EPICS at 25 °C

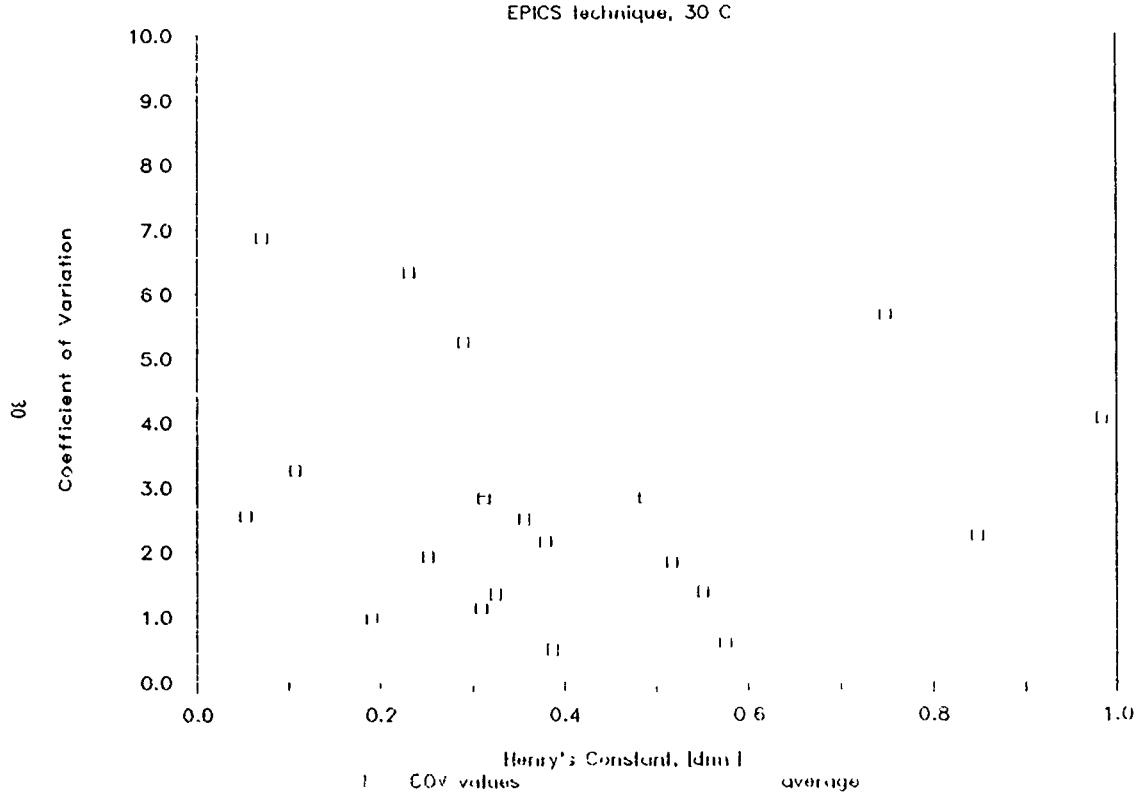

Figure 7. Coefficient of Variance Values vs. Henry's Constant for the EPICS at 30 °C

TABLE 10. COEFFICIENT OF VARIATION VALUES FOR THE 51 ORGANIC CHEMICALS OF INTEREST

Number	Component name	Coefficient of variation, %				
		10 °C	15 °C	20 °C	25 °C	30 °C
1	Nonane*	15 59	19.64	62 98	22 13	61 56
		3 99	14 85	18.03	26 69	29 63
2	Hexane	40 01	15 87	19 19	18 61	31 65
3	2-Methylpentane	23 49	15 31	18 00	16.31	79.75
		18 99	19.10	69.26	88.64	66 41
4	Cyclohexane	1 76	7.03	11 47	4.39	2 61
5	1,2-Dichlorobenzene	12 19	7.63	4.29	8.56	10 56
		33.04	39.24	11.05	11.32	4.12
6	Chlorobenzene	7 23	1.00	1.60	0.76	3.97
7	1,3-Dichlorobenzene	9 48	5.99	3.81	0 59	4 16
		16.52	16.97	19.71	20.19	4 92
8	1,4-Dichlorobenzene	5 03	5.59	4.08	8.35	9 17
		21.53	13 64	16.66	1.69	10 09
9	o-Xylene	5.30	5 04	5.62	2.11	1.93
10	p-Xylene	5.18	4 13	2.51	1.90	2 14
11	m-Xylene	4.71	2 31	3.01	4 67	2 50
12	Propylbenzene	3.45	4.82	1.24	2.62	1 38
13	Ethylbenzene*	7.48	2 97	4.71	1.42	4.48
		0.63	5 64	3.46	2 97	2 28
14	Toluene	5.26	7.83	2.31	0.60	1 34
15	Benzene	1.50	6 35	4.83	4.72	5 24
16	Phenol	6.02	9 57	53.81	5.52	5 67
17	Methyl ethylbenzene	1.66	2 38	3.61	1.97	1 12
18	1,1-Dichloroethane	2.43	2 66	1 92	1 21	2 82
19	1,2-Dichloroethane*	7.49	1.23	1 91	1 93	2 42
		4 37	4.06	7.81	1 67	6 87
20	1,1,1-Trichloroethane	2.98	5.51	0 58	1 35	2 24
21	1,1,2-Trichloroethane*	11.24	6.24	5.12	10 91	9 18
		25.79	7.41	8 64	8.82	2.55
22	cis-Dichloroethylene	3.80	4.26	0.17	4 00	6.32
23	trans-Dichloroethylene	5.24	0.79	4.48	1.30	2.82
24	Tetrachloroethylene	4.19	4.99	1.52	1 65	4.04
25	Trichloroethylene	3.65	4.41	3.72	1 25	1.84
26	Naphthalene	30 57	74.63	12 93	29 07	6.50
27	Tetralin*	35 68	9 98	10.94	5.80	10.34
		38 85	30 24	17.79	10.03	3 26
28	Decalin*	6.96	7 74	4.97	6.79	13 94
		17 41	9.34	5.76	3.19	27.78
29	Anthracene	--	--	--	--	--
30	Vinyl chloride	3.89	6 31	9.12	6.18	19.09
		1.27	1 63	0 62	1.24	2.97
31	Chloroethane	3.50	1.50	0.99	1.46	0.59
32	Hexachloroethane	5 28	7.23	21.26	1.48	4 66
		43.20	8.65	4.61	14.83	21 65

*For these components, the 2 values listed represent replicate tests.

(continued)

TABLE 10 COEFFICIENT OF VARIATION VALUES FOR THE 61 ORGANIC CHEMICALS OF INTEREST (concluded)

Number	Component name	Coefficient of variation, %				
		10 °C	15 °C	20 °C	25 °C	30 °C
33	Carbon tetrachloride	1.28	3.90	3.41	2.25	5 93
34	1,3,5-Trimethylbenzene	4.52	1 89	4.81	2.70	0,48
35	bis(2-Ethylhexyl) phthalate	--	--	--	--	--
36	Ethylene dibromide*	45.73	7 01	12.23	5.30	16.53
		33.19	49.30	52 61	5.41	7.28
37	1,1-Dichloroethylene	3.41	17 22	3.09	2.67	0.89
38	Methylene chloride*	6.99	1.54	4.83	2.56	1.67
		9.04	0.98	4.28	3.32	2.37
39	Chloroform*	4.13	2.51	2.35	5.22	7 24
		2.35	10.37	2.05	3.63	2.04
40	1,1,2,2-Tetrachloroethane	45.57	53 06	34.56	86.05	56.56
41	1,2-Dichloropropane	1.12	9.54	6.49	26.57	15.31
42	Dibromochloromethane	33.91	37.20	6 20	2 72	4.22
43	1,2,4-Trichlorobenzene	39.03	51.33	7.41	6.18	21.95
44	2,4-Dimethylphenol	22.72	12 99	19.28	10.40	6.17
45	1,1,2-Trichlorotrifluoroethane	5.63	8.21	7.40	5.60	3.00
46	Methyl ethyl ketone (MEK)*	119.86	41 57	27.74	1 12	32.58
		35 50	21.40	6.32	81.79	19 78
47	Methyl isobutyl ketone (MIBK)*	28.47	2.80	36.36	36.14	11 55
		60.64	18 25	18.49	19.09	28.96
48	Methyl cellosolve	33.20	16.07	32.33	16.03	15.85
49	bis(2-Chloroethyl) ether	75 96	347 46	28.41	92.84	697.60
50	Trichlorofluoromethane	6.47	0.57	1.07	1.75	3.86
51	2,6-Dinitrotoluene	--	--	--	--	--
	Average =	17.46%	17.64%	12.18%	12.16%	22.46%

TABLE 11 HENRY'S CONSTANTS (IN kPa-m^3/gmol) FOR 51 ORGANIC CHEMICALS

Number	Component name	10 °C	15 °C	20 °C	25 °C	30 °C
1	Nonane*	34 0104	39.8141	79.9291	48 8644	84.7429
		40.5496	50.2737	33.5974	41.9658	47.0755
2	Hexane	24.1652	41.9006	89 4293	77.7670	158.2690
3	2-Methylpentane *	70.6713	70.2823	64.0931	83.5673	85.9688
		83.1849	20.6253	20.5385	70.6641	320.1020
4	Cyclohexane	10.4229	12.7312	14 1413	17.9496	22.5798
5	1,2-Dichlorobenzene *	0 1648	0.1453	0.1703	0 1590	0.2402
		0 1231	0.1111	0.2065	0 1875	0.2709
6	Chlorobenzene	0.2477	0.2848	0.3455	0.3645	0.4795
7	1,3-Dichlorobenzene *	0.2244	0.2341	0.2976	0 2890	0.4276
		0.1194	0.2384	0.2956	0.3053	0.3782
8	1,4-Dichlorobenzene *	0.2148	0.2200	0.2622	0.3212	0.3940
		0.1650	0.2181	0.2517	0.2876	0.4050
9	o-Xylene	0.2891	0.3661	0.4803	0.4930	0.6343
10	p-Xylene	0.4259	0.4897	0.6537	0.7538	0.9572
11	m-Xylene	0 4161	0.5028	0.6057	0.7638	0.8991
12	Propylbenzene	0.5756	0.7407	0.8926	1 0906	1.3868
13	Ethylbenzene *	0.4478	0.6622	0 7448	0.8024	1.0425
		0.3303	0.4569	0.6088	0.7986	1.0680
14	Toluene	0.3863	0.4988	0 5821	0 6503	0.8183
15	Benzene	0 3345	0.3936	0.4579	0 5345	0.7297
16	Phenol	0.6058	0.8272	0.9928	1.3032	1.8852
17	Methyl ethylbenzene	0.3552	0.4253	0.5100	0.5655	0.7807
18	1,1-Dichloroethane	0.3726	0.4601	0.5708	0.6334	0 7867
19	1,2-Dichloroethane *	0 1184	0.1316	0.1492	0.1430	0 1767
		0 0714	0.0890	0.1229	0.1477	0 1777
20	1,1,1-Trichloroethane	0.9774	1 1668	1.4802	1.7620	2.1367
21	1,1,2-Trichloroethane *	0.1178	0.1010	0.1234	0.1063	0.1270
		0.0397	0.0539	0.0751	0.0920	0 1348
22	cis-Dichloroethylene	0.2740	0.3304	0.3643	0.4605	0 5823
23	trans-Dichloroethylene	0 5995	0.7140	0.8679	0.9575	1 2293
24	Tetrachloroethylene	0.8576	1.1268	1.4239	1.7278	2.4793
25	Trichloroethylene	0.5452	0.6763	0.8530	1.0296	1.3011
26	Naphthalene	0.2601	0 0298	0.0629	0 1225	0.0825
27	Tetralin *	0.3294	0.1734	0.1952	0.1706	0.2702
		0 0757	0 1066	0.1373	0.1691	0.2717
28	Decalin *	7.0927	8.4812	10.6979	11.8355	20.1293
		6.6201	7 8464	9 8884	13.3147	23.0922
29	Anthracene	--	--	--	--	--
30	Vinyl chloride *	1.0606	1.3185	1.4683	2 2402	1 7869
		1.5200	1.7017	2.2030	2.8835	2 8414
31	Chloroethane	0.7693	0.9710	1 1128	1.2274	1 4484
32	Hexachloroethane *	0.6007	0.5681	0.5991	0 8467	1.0463
		0.2168	0.7376	0 5877	1.0505	0 9083
33	Carbon tetrachloride	1.5035	1.9366	2.3545	2 9837	3.8338
34	1,3,5-Trimethylbenzene	0.4089	0.4657	0.5789	0.6822	0.9754
35	bis(2-Ethylhexyl) phthalate	--	--	--	--	--
36	Ethylene dibromide *	0.1254	0.0644	0.0472	0.0534	0 0795
		0.0306	0.0483	0 0614	0.0662	0.0806

(continued)

TABLE 11. HENRY'S CONSTANTS (IN kPa-m^3/gmol) FOR 61 ORGANIC CHEMICALS (concluded)

Number	Component name	10 °C	15 °C	20 °C	25 °C	30 °C
37	1,1-Dichloroethylene	1.5580	2 0584	2.2054	2.6205	3.2180
38	Methylene chloride *	0.1414	0.1713	0.2473	0.3003	0.3659
		0.1643	0.1919	0.2262	0.3813	0.3530
39	Chloroform *	0.1746	0 2368	0.3363	0.4263	0.5614
		0 2345	0 2942	0.3784	0 4901	0.5968
40	1,1,2,2-Tetrachloroethane	0.0335	0.0201	0.0743	0.0253	0.0709
41	1,2-Dichloropropane	0.1240	0.1281	0.1926	0 3621	0.2901
42	Dibromochloromethane	0.0383	0 0461	0 1046	0 1197	0.1542
43	1,2,4-Trichlorobenzene	0.1305	0.1068	0 1852	0.1950	0.3011
44	2,4-Dimethylphenol	0.8402	0.6827	1.0273	0.4999	0.3802
45	1,1,2-Trichlorotrifluoroethane	15.5712	21.8026	24.7009	32.3154	32.5372
46	Methyl ethyl ketone (MEK) *	0 0168	0 0230	0.0250	0.0248	0.0297
		0.0282	0.0397	0.0188	0.0131	0.0112
47	Methyl isobutyl ketone (MIBK)*	0.0687	0.0377	0.0291	0.0594	0.0687
		0.0125	0.0116	0.0106	0.0198	0.0159
48	Methyl cellosolve	4.4700	3.8781	11.7125	3.1338	3.8631
49	bis(2-Chloroethyl) ether	0.1264	0.0160	0.0730	0.0127	0.0014
50	Trichlorofluoromethane	5.4263	6.8878	8.1459	10.2635	12.3386
51	2,6-Dinitrotoluene	--	--	--	--	--

* Note: Components with two entries represent replicate tests (see page 19 of text).

TABLE 12. COMPARISON OF SELECTED RESULTS WITH OTHER REPORTED VALUES
(Henry's Constant Expressed in atm-m3/mol at 25 °C)

Compound	H[a]	H[b]	H[c]	H[d]	H[e]	H[f]
Cyclohexane	5.46E-02[g]	1.77E-01	1.91E-01		3.28E-03	1 43E-02
Chlorobenzene		3.68E-03	3.46E-03			5 41E-03
o-Xylene		4.87E-03	4.93E-03			8.83E-03
p-Xylene	7.525E-03	7.44E-03	7.00E-03			1 17E-02
m-Xylene		7 44E-03	8.91E-03			1.10E-02
Propyl benzene		1.00E-02	8.91E-03			8.51E-03
Toluene		6.42E-03	8 81E-03		6.39E-03	8.13E-03
Benzene	5.8E-03	5.28E-03	5.42E-03		5 47E-03	5.45E-03
Phenol		1.20E-02				
Methyl ethylbenzene	7.39E-03	5.59E-03	4.91E-03			9.46E-03
1,1-Dichloroethane		6.26E-03	5.78E-03	5.62E-03		4.27E-03
1,2-Dichloroethane	6.28E-04	1.48E-03	1.22E-03			2.08E-02
1,1,1-Trichloroethane	1.76E-02	1.74E-02	3 02E-02	1.72E-02	2.00E-02	
1,1,2-Trichloroethane	1.12E-03	1 05E-03	1.21E-03		8.28E-04	1.53E-03
cis-Trichloroethylene	4.54E-03	7.51E-03	4.09E-03			
trans-Dichloroethylene	9.45E-03	6.61E-03	9.38E-03			
Tetrachloroethylene	1.86E-02	1.07E-02	2.90E-02	1.77E-02	1.60E-02	1.88E-03
Trichloroethylene		1.02E-02	1 10E-02	9.58E-03	9.72E-03	2.23E-03
Tetralin		1.69E-03				2.99E-03
Chloroethane		1.21E-02	1.13E-02	1.11E-02		4 99E-03
Carbon tetrachloride	2.94E-02	1.56E-02	3.04E-02	2.74E-02		2.76E-02
1,3,5-Trimethylbenzene	8.38E-03	6.73E-03	5 92E-03			1.44E-02
1,1-Dichloroethylene	2.8E-03	2.58E-02	1.31E-01	2.61E-02	3.68E-02	

[a]Bubble column this study.
[b]EPICS, this study (raw data).
[c]Reference 2.
[d]Reference 7.
[e]Reference 8.
[f]Reference 9 and Reference 10.
[g]Nonequilibrium measurement.

reported values of Henry's constants to vary by several orders of magnitude. For example, experimental results for vinyl chloride suggest a Henry's law constant of approximately 2.21 by 10^{-2} atm by m^3/mol at 25 °C, while values of 2.3 by 10^{-2} to 6.39 atm by m^3/mol are reported by Mackay and Shiu (Reference 2) and Goldstein (Reference 11). Large uncertainties in the absolute aqueous solubility probably contribute most to these discrepancies.

The comparison of the EPICS results from this study to those of Gossett (Reference 7) are quite good. Again, both positive and negative differences were observed; however, all values agreed within 10 percent. This close agreement demonstrates how reproducible results are between investigators using the EPICS technique.

Leighton and Calo (Reference 8) used an equilibrium cell with continuous gas flow, followed by direct analysis of both the air and water phases to determine Henry's constants. Of the nine compounds common to both studies, results for six of the compounds agree reasonably well (within 10 percent). Larger differences are observed for the other three compounds (1,1,1-trichloroethane, 1,1,2-trichloroethane, and 1,1-dichloroethylene). Both positive and negative differences (15 to 42 percent) were noticed. This difference can be explained by the analytical problems discussed in Leighton's study and is not an artifact of the EPICS procedure.

The UNIFAC (UNIFAC Functional Group Activity Coefficient) model was developed in 1975 to correlate large quantities of data with a relatively few molecular parameters. The first group contribution technique developed for activity coefficient prediction was that of Wilson and Deal (Reference 12); the subsequent development of UNIFAC by Fredenslund et al. (Reference 3) owes much to their early work. The theoretical aspects of UNIFAC are discussed in detail in Section VI.

By employing the UNIFAC model to calculate activity coefficients for the compounds of interest in a dilute aqueous solution, one may then use Equation (7) in conjunction with pure component vapor pressure data to calculate Henry's law constants. Values obtained in this fashion are shown in the last column of Table 12. A limitation of this approach is that the binary interaction parameters tabulated by Gmehling et al. (Reference 13) were not derived from data in the extremely dilute region. As a result, extrapolation to infinite dilute may lead to large errors, as seen for cyclohexane or tetrachloroethylene.

Generally speaking, the EPICS results from this study agree well with other published results. However, for most of the compounds reported here, reliable values of Henry's constant do not exist in the literature, and if they do, values are rarely reported as a function of temperature with rigorous statistics. The EPICS procedure proved to be a simple and accurate technique for determining Henry's law constants for a variety of organic chemicals. The constants reported have numerous environmental applications (fate and transport models, remedial action plans) and are within the 10 percent accuracy suggested by Mackay and Shiu (Reference 2).

SECTION IV

SOLUBILITY MEASUREMENTS

A. INTRODUCTION

Solubility data for organic compounds in water are important for environmental studies because they provide fundamental information necessary to predict transport in aqueous systems. This data may also be used to predict carbon adsorption of contaminants, and the air or steam stripping behavior for a given organic. For highly soluble materials these data are readily obtained by methods as simple as weight measurements; however, precise determination of solubility limits is difficult for sparingly soluble compounds, requiring tedious methods such as radio labelling (Burris and MacIntyre, Reference 14) to obtain precise results. Rarely is any temperature dependency data available for solubility; therefore, in this report, aqueous solubility of the 51 tests chemicals is reported at 10 °C, 20 °C, and 30 °C.

Three methods dominate the current literature--nephelometry, the shake-flask method, and the generator column--and each has specific limitations. Nephelometry differs from the latter two in that the measurement employed is indirect. Mixtures of water and the solute of interest are made for several known dilutions. These mixtures are agitated vigorously, using either mechanical shakers or ultrasonic devices to produce a total suspension of the solute in water. The turbidity of these mixtures is then determined optically for a succession of solute dilutions and plotted as a function of the known concentration of these dilutions. The line obtained is extrapolated to zero turbidity. The concentration at that point is taken as the solubility limit of the solute. Hollifield (Reference 15) reports 95 percent confidence limits of between 5 and 20 percent, with decreasing accuracy for less soluble materials, using this method. However, the employed surfactants and other materials to achieve uniform emulsions. Because of the poor accuracy for highly insoluble chemicals, most researchers have chosen to use the shake-flask or column generator method to determine the solubilities of these compounds.

In the shake-flask method, a known amount of solute is added to a measured water sample in a sealed container. The amount of solute is chosen to exceed the anticipated solubility limit. This mixture is shaken or stirred and allowed to sit for 8 hours to several days to ensure that solute-solvent equilibrium is obtained. The mixture is then filtered or centrifuged to remove suspended solute particles, and the concentration in the remaining solution is determined.

Two basic methods may be used to determine the resulting aqueous concentration. One method is to employ Henry's law and the measurement of the gas-phase concentrations in the headspace to determine the aqueous concentration.

The gas-phase concentration of the solute is determined for the saturated solution and divided by the Henry's law constant to obtain the aqueous solubility limit.

The second method of determining the aqueous concentration involves extracting the dissolved material from a known volume of water and determining the amount of materials recovered. The water solution is passed through a sorbent material bed to remove any organic-solute material; and this sorbent, in turn is, extracted using an organic solvent such as hexane. The resulting concentrated solute is measured using a spectrophotometer and liquid chromatograph.

The column generator and related high-pressure liquid chromatograph (HPLC) methods of determining aqueous solubility are the most recent of the three described. However, it has become the predominant method in the literature over the past 5 years. In this method, a column is packed with an inert solid material, such as fine silica powder (100 to 120 mesh), that serves as a support for the organic-solute phase. The fine powder provides a high surface area for the solute to ensure rapid equilibration between it and the aqueous phase. The support is impregnated by flooding the column with the solute of interest and letting it sit for several hours. Water is then admitted to push the plug of the organic phase from the column. The column is brought to the desired temperature by appropriate controls and flushed with water until the presence of undissolved solute is not detected. To ensure that equilibrium between the solute and the aqueous phase is achieved, the outlet concentration as a function of flow rate should be determined for each compound of interest. Ultraviolet, infrared, or spectrofluorescence detectors may be incorporated into the HPLC to determine the solute concentration in each eluted phase. The point at which the solute concentrations become flow-independent represents the maximum water flow rate allowed through the column and should also represent the equilibrium concentration.

The shake-flask method has four major sources of determining error associated with it. The first of these stems from the organic-solute losses due to adsorption of the solute on the flask walls or to evaporation. This quantity is somewhat dependent on the vapor pressure of the solute, but if the quantity of the solution used is fairly large (i.e., 250 mL), these losses are usually minimized to 5 percent of the total solute. The second error source is undissolved solute suspended in the water phase. This emulsion may cause a sample to register an anomalously high solubility. Centrifugation or filtration should reduce this false contribution. The third source arises from the extraction efficiency for the removal of solute from water using an organic solvent, a technique common to most methods. Finally, the accuracy of the detection method contributes to the overall error in this method.

The column method also has several steps that may result in a negative bias on the measured aqueous solubility. The lack of water-solute equilibrium in the generator column itself may produce an outlet concentration lower than the "true" solubility. Stolzenburg and Andren (Reference 16) define this certainty to approach 95 percent over a tenfold decrease in flow rates. The efficiencies for the adsorption and extraction steps and the detection limitations may be estimated to be similar to the shake-flask efficiencies.

Other problems are attendant to the column method. If the solubility of the organic phase is greater than approximately 1000 ppm, the stationary phase on the support depletes rapidly, and a steady-state effluent concentration may not be obtained. A large portion of chemicals in this study have solubilities in and above that range. Second, some strong UV adsorbers (principally aromatic compounds) may preferentially plate out on the UV detection cell window. This causes a significant signal drift during the course of a single measurement. Finally, to achieve accurate calibration of the UV results and to avoid underestimation, shake-flask samples of known concentration must be prepared. This eliminates most of the proposed advantages of the generator column technique.

B. EXPERIMENTAL

Initially, all three of the principal measurement methods were examined: nephelometry, generator column, and shake flask. The results for some of the compounds were compared for the different methods. By far, the most satisfactory method turned out to be the shake-flask method. All the final results reported for the solubility measurements are measured by this method. First, the outcome of the nephelometry and generator column trials are discussed.

1. Nephelometry Measurements

During a preliminary investigation designed to test nephelometric methods for reproducibility and consistency with literature values, it became apparent that nephelometry may not be suitable for this purpose. Predicted values for solubility limits were consistently high when compared to literature values, experimental reproducibility was poor at best, and the relationship between light-scattering and organic concentration appears to be linear only in a very limited range.

During experimentation, it appeared that loss of suspended organics to the atmosphere and to glass surfaces were significant sources of error. Droplets of organic material were observed to adhere to the surface of the glass sample containers, even while placed in a sonicating bath. Although length of storage in a closed container did not (for nonreactive components) appear to alter eventual turbidity readings, successive readings taken from the same flask yielded decreasing extents of turbidity. This indicates loss of volatile organics to the atmosphere. In addition, after short periods of time in a cuvette, turbidity gradients were evident, possibly indicating the tendency of dispersed organic particles to coalesce.

It was also observed that the assumption of detector linearity is valid in a certain region only. This is to be expected because linearity implies uniform particle size, when in reality, a size distribution exists. This particle-size distribution is a function of the rate of coalescence, which in turn depends on the concentration of the dispersed phase. In addition, the distribution is dependent on the properties (e.g., surface tension) of the organic phase in solution, so the length of the linear range varies from one compound to another. As a result, each compound must be examined independently before linearity can be assumed.

Preliminary findings indicate that the nephelometric methods employed are not sufficiently accurate to warrant their use in checks of experimentally determined solubilities, in the more dilute solutions. However, the solubilities of several high solubility compounds on the Air Force list were checked using nephelometry. This method was employed for phenol, toluene, cis-dichloroethylene, trans-dichloroethylene, methyl ethyl ketone, methyl isobutyl ketone and trichloroethylene. The solutions were prepared at several concentrations well above the anticipated solubility limit in 100 mL volumetric flasks. These flasks were immersed in a temperature-controlled ultrasonic bath and sonicated until the organic was completely dispersed (2 to 8 hours). Samples were poured into couvettes, and the turbidity was then determined by a Hach 2100A turbidimeter calibrated with standard (NTU) solutions. The measured turbidity was plotted as a function of the mixture concentration for several dilutions. The plot is extrapolated to zero turbidity using a least-squares fit, and the concentration at that point is used as the solubility limit. This technique has a fairly low accuracy and may only be applied adequately to those compounds with a solubility of over 5000 ppm. The nephelometry results for some of these sample compounds are shown in Table 13. Although the method will yield rough estimates of solubilities, it is certainly not accurate enough to predict changes in solubilities over small (10 °C) temperature intervals.

TABLE 13. NEPHELOMETRY RESULTS

Compound	Temperature, °C	Solubility, ppm	Correlation coefficient
Toluene	30	673.9	0.989
	20	601.3	0.984
	10	618.9	0.968
trans-Dichloroethylene	30	6594	0.970
	20	6055	0.998
	10	5274	0.995
cis-Dichloroethylene	30	3025	0.970
	20	3126	0.960
	10	2572	0.965
Trichloroethylene	30	1282	0.950
	20	1250	0.910
	10	1271	0.825

2. Generator Column

The major focus of work performed in this phase of the project was on determining the accuracy and reliability of the HPLC-generator column method for measuring solubilities. Toluene was chosen as the initial chemical to be

tested because it has a reported solubility in the median range of the chemicals to be analyzed and is a fairly common chemical. Its solubility limit has been reported in several literature references and it is also safe and inexpensive. The experimental procedure included testing various HPLC packing materials, varying flow rates, varying column loading techniques, and determining the most accurate methods of calibrating the UV detector. Testing was done using a Varian 5000 HPLC unit equipped with a UV-50 Variable Wavelength Detector.

The packing materials used included treated and untreated Chromosorb P and glass beads. The packing materials seemed to have little effect on the height of the equilibrium plateau attained from the analysis. Changing the flow rate from 0.5 cc/minute to 2.0 cc/minute also has no effect on the signal height. The equilibrium value also did not seem to vary with the amount of water added to the column when it was being loaded, as long as the concentration was well above the solubility limit. The major problem encountered was in calibrating the signal height to the precise concentration it represents.

Many methods were used to prepare and analyze calibration standards of known concentrations. The standards were prepared in varying concentrations to obtain a linear response from the UV detector of peak height versus concentration. The results of this study indicated that the major drawback to this method was calibration. The effort put into producing reliable standards was much greater than that required to produce the saturated solutions. This is discussed in greater length in the following section for the shake-flask experiments.

In addition, for those compounds with solubility in excess of approximately 1000 ppm, a steady state was difficult to achieve for long periods. The UV detector response would increase initially with the introduction of the HPLC flow through the stationary phase. However, after a short time (less than 5 minutes), the UV response would drop as the stationary phase was depleted. Larger columns saturated with the stationary phase might solve this problem, however, the technique as described in the literature would probably only be applicable to less than half of the test materials of this study.

3. Shake Flask Measurements

The primary method of determining aqueous solubilities in this study was the shake-flask method. Although its concept is extremely simple, the actual measurements require extremely accurate laboratory procedures to reduce error. The shake-flask method has been applied to all of the original compounds except vinyl chloride (gas).

Calibration standards of known concentrations of the compound of interest are prepared in 250-milliliter (±1 mL) amber bottles fitted with double Teflon® lined septa. The bottles are initially filled with distilled, deionized water and sealed so as to leave zero headspace. The organic liquids

are measured volumetrically and injected through each septum using a microliter syringe. Conversion of parts per million by volume to parts per million by weight is done by multiplying the former by the sample density (at 25 °C). Solid samples, such as 1,4-dichlorobenzene or naphthalene, are weighed on a Mettler microbalance and added to the water before sealing the septum. The saturated samples are prepared by adding organics far in excess of the anticipated solubility limit so that a distant organic layer is formed. Once the samples are prepared, they are shaken for 1 hour with a wrist-action shaker and then allowed to rest until fully dissolved or equilibrated. This equilibration takes approximately 3 weeks, on average.

The concentration measurements for the samples are performed in two ways. For those compounds that have a strong UV adsorbance, such as the aromatic compounds, the samples are injected into a LDC UV III Monitor (256 nm), and the UV adsorbance for a particular concentration of organic is determined. A calibration plot is made of concentration versus adsorbance for all of the independently prepared calibration samples (4 to 5 samples). The saturated solution, which has been equilibrated at 10 °C, 20 °C, or 30 °C is then measured for adsorbance in the same way as the calibration standards. The concentration of the saturated solution is then determined for the extrapolation of the calibration line.

A second measurement method is employed for those compounds that are weak UV absorbers. The calibration samples are prepared in methanol to concentrations in the range of the expected solubility limit in water. These samples are then injected directly into a GC equipped with an 80/120 Carbopack B/3 percent SP-1500 column (1.8 inch inner diameter by 10 feet) and a FID detector. Once again, a calibration plot of GC response versus concentration is prepared. A saturated aqueous solution at 10 °C, 20 °C, or 30 °C is then injected and the GC response compared to the plot to obtain the ultimate solubility concentration.

The utility of this dual approach may be demonstrated for naphthalene. Naphthalene has a solubility in the low ppm range. Calibration standards of 1 ppm are detectable in the gas chromatograph, but extremely long retention times (>1 hour) are demonstrated on any water-tolerant columns. On the other hand, naphthalene has a very strong UV adsorbance in this concentration range and may be measured accurately and rapidly. Compounds such as n-hexane have virtually no UV adsorption and are, therefore, not amenable to this technique. Gas chromatography, therefore, becomes the method of choice.

The results of the shake-flask tests are shown in Table 14. This table summarizes the aqueous solubilities determined for the test compounds for all three temperatures and the method of measurement used for each. A detailed presentation of the calibration tests and 95-percent confidence bands are shown in Appendix C. There were three compounds for which solubility results could not be obtained, most probably because their solubility was below the limits of detection: n-nonane, decalin, and 1,2-dinitrotoluene. In addition, results for the gaseous compounds, vinyl chloride and chloroethane are not available due to the difficulties in assuring complete saturation of the gas in water, as well as the safety hazard associated in doing complete

TABLE 14. LIST OF SOLUBILITY RESULTS

Component number	Component name	Solubility, ppmw 10 °C	20 °C	30 °C	Method of detection
1	n-Nonane	nd	nd	nd	--
2	n-Hexane	42	47	47	G.C.
3	2-Methylpentane	25	19	16	G.C.
4	Cyclohexane	43	47	49	G.C.
5	1,2-Dichlorobenzene	186	182	176	U.V.
6	Chlorobenzene	411	441	464	U.V.
7	1,3-Dichlorobenzene	176	159	145	U.V.
8	1,4-Dichlorobenzene	98	89	91	U V.
9	o-Xylene	184	194	202	U.V
10	p-Xylene	186	196	200	U V.
11	m-Xylene	179	186	199	U.V.
12	Propylbenzene	53	60	62	U V.
13	Ethylbenzene	100	107	121	U.V.
14	Toluene	575	577	588	U.V.
15	Benzene	1822	1800	1872	U.V.
16	Phenol	7.8pph	7.9pph	8.4pph	Nephelometry
17	Methyl ethylbenzene	220	229	231	U.V.
18	1,1-Dichloroethane	7435	7137	6130	G C
19	1,2-Dichloroethane	10554	8467	10467	G.C.
20	1,1,1-Trichloroethane	1399	1559	1420	G.C.
21	1,1,2-Trichloroethane	4659	4527	4177	G.C.
22	cis-Dichloroethylene	152	273	176	G.C.
23	trans-Dichloroethylene	4188	3580	3851	G.C
24	Tetrachloroethylene	99	136	116	G.C.
25	Trichloroethylene	1499	1194	1401	G.C.
26	Naphthalene	35	38	39	U.V.
27	Tetralin	434	455	471	U.V.
28	Decalin	nd	nd	nd	--
29	Anthracene	20ppb	20ppb	20ppb	U.V.
30	Vinyl chloride	--	--	--	--
31	Chloroethane	--	--	--	--
32	Hexachloroethane	41	37	41	G.C.
33	Carbon tetrachloride	104	146	105	G.C.
34	Mesitylene	107	109	112	U.V.
35	bis(2-Ethylhexyl) phthalate	1	1	1	U.V.
36	Ethylene dibromide	3731	3471	2397	G.C.
37	1,1-Dichloroethylene	630	750	656	G C.
38	Methylene chloride	11092	13508	11211	G.C.
39	Chloroform	3471	2983	3598	G.C.
40	1,1,2,2-Tetrachloroethane	2588	2526	2131	G C
41	1,2-Dichloropropane	2052	2030	1867	G.C.
42	Dibromochloromethane	3040	2375	3182	G.C.
43	1,2,4-Trichlorobenzene	41	36	39	U.V.
44	2,4-Dimethylphenol	34786	35648	37549	Nephelometry
45	1,1,2-Trichlorotrifluoroethane	38	37	14	G.C.

(continued)

TABLE 14. LIST OF SOLUBILITY RESULTS (concluded)

Component number	Component name	Solubility, ppmw 10 °C	20 °C	30 °C	Method of detection
46	Methyl ethyl ketone	27 5pph	32 6pph	34 5pph	G.C.
47	Methyl isobutyl ketone	19100	21560	22315	G.C.
48	Methyl cellosolve	--	Miscible	--	--
49	bis(2-Chloroethyl) ether	9799	10110	10216	G C.
50	Trichlorofluoromethane	541	341	262	G C.
51	2,6-Dinitrotoluene	nd	nd	nd	--

saturation studies. For the sake of comparison, a compendium of literature values for many of the compounds is shown in Table 15.

Comparing these literature values to the ones obtained in the current work, no clear tendencies (either high or low) are statistically evident. However, it should be noted from the 95 percent confidence bands listed in Appendix C that in most cases the temperatures dependence is not statistically significant. This is chiefly due to the fact that solubilities are not a strong function of temperature. Also, in examining the results noted that seldom are the solubilities observed to be monotonic with temperature. Although the effect of temperature in these studies is often not statistically significant, three general trends may be observed. First, the solubility of the halogenated hydrocarbons decreased with temperature. Second, the solubility of the substituted aromatic hydrocarbons increases with temperature. Finally, maxima and minima are observed for a wide range of compounds without any general trend that can be demonstrated to be statistically significant. More detailed temperature studies for these systems need to be conducted before conclusions as to their origin may be drawn. A full outline of the statistical analysis is given in the data analysis discussion of Section VI.

TABLE 16. COMPILATION OF AQUEOUS SOLUBILITIES FROM THE LITERATURE FOR ORGANIC COMPOUNDS OF INTEREST TO THE AIR FORCE

Compound	Solubility ppm, 25 °C	FW	Density, g/mL	bp, °C	Reference
p-Xylene	185	106.17	0.866	138	2
	214				17
m-Xylene	162	106 17	0.868	138	2
	160				17
o-Xylene	175	106.17	0 897	144	2, 18
	220				17
	204				18
Toluene	515	92.14	0 867	111	2, 15
	533 (15 °C)				19
	557				19
	587 (35 °C)				19
	635 (45 °C)				19
	670				20
	570				17
	530				18
	627				18
	470				18
	536				18
Phenol	8.2 pph	94.11	1 071	181	2
Ethylene dibromide	--	187.87	2.180	131	
bis(2-Ethylhexyl)phthalate	--	390.56	0.981	384	
Chlorobenzene	471	112.56	1 106	132	2
	293				17
	474				21
1,2-Dichlorobenzene	123	147.00	1 305	178	2
	149				21
1,3-Dichlorobenzene	--	147.00	1.288	172	
	149				20
	125.6				21
1,4-Dichlorobenzene	83	147.00	1 241	173	2
	92.1				21
cis-Dichloroethylene	3500	96 94	1.284	60	2

(continued)

TABLE 15. COMPILATION OF AQUEOUS SOLUBILITIES FROM THE LITERATURE FOR ORGANIC COMPOUNDS OF INTEREST TO THE AIR FORCE

Compound	Solubility ppm, 25 °C	FW	Density, g/mL	bp, °C	Reference
trans-Dichloroethylene	6300	98.96	1 257	48	2
1,1-Dichloroethane	400	98.96	1 177	57	2
	4834				21
1,2-Dichloroethane	8700	98.96	1.256	83	2
1,1,1-Trichloroethane	720	133.41	1 435	75	2
	1150				20
1,1,2-Trichloroethane	720	133.41	1 435	112	2
1,1-Dichloroethylene	400	96.94	1.013	31	2
Tetrachloroethylene	140	165.83	1.623	121	2
Trichloroethylene	1100	131 39	1.462	87	22
	1470				
Carbon tetrachloride	1160	153.82	1 594	77	2
Cyclohexane	55	84.16	0.779	81	2, 18
	52				20
	63				32
n-Hexane	10	86.18	0.659	69	2
	12				17
	9.5				18
	140				33
	36				32
	55.6				22
2-Methylpentane	78	86.18	0 653	62	2
1,3,5-Trimethylbenzene	97.48	120.20	0.864	163	2
	57				18
	57.6				22

(continued)

TABLE 16. COMPILATION OF AQUEOUS SOLUBILITIES FROM THE LITERATURE FOR ORGANIC COMPOUNDS OF INTEREST TO THE AIR FORCE

Compound	Solubility ppm, 25 °C	FW	Density, g/mL	bp, °C	Reference
Propylbenzene	55	120.20	0.862	159	2
	42.6 (15 °C)				34
	42.5 (20 °C)				34
	43.2				34
	44.5 (30 °C)				34
	52				17
	50				18
	73				18
	50.1				22
Methylethylbenzene	93	120.20	0.867		2
Vinyl chloride	334	62.50	2.58 x 10^{-3} (g)	12	2
	403 (0.2 °C)				23
	143				23
	68 (50 °C)				23
Chloroethane	5710	64.52	2.67 x 10^{-3} (g)	12	2
Hexachloroethane	500	236.74	2.091	193(mp)	2
	27.2				22
Benzene	1780	78.11	0.874	80	2, 18
					24, 25
	1540 (15 °C)				19
	1610				19
	1760 (35 °C)				19
	1850 (45 °C)				19
	1880				20
	1779.5				26
	1791				27
	1755				28, 29
	1796				30
	1740				31
	1450				32

(continued)

TABLE 15 COMPILATION OF AQUEOUS SOLUBILITIES FROM THE LITERATURE FOR ORGANIC COMPOUNDS OF INTEREST TO THE AIR FORCE

Compound	Solubility ppm, 25 °C	FW	Density, g/mL	bp, °C	Reference
Ethylbenzene	152	106.17	0 867	136	2, 18
	176 (15 °C)				19
	181				19
	194 (35 °C)				19
	215 (45 °C)				19
	166				17
	168				18
	208				18
	140				18
	165				18
Naphthalene	34	128.17	0.997	81(mp)	2
	31.7				35
	34.4				36, 37
	31.69				27
	30.3				38
	31.2				39
Tetralin	--	132.21	0.973	207	
Decalin (cis)	--	138.25	0.897	193	
Anthracene	0.07	178.23	1.283	340	2
	0.073				35
	0.075				30, 39
	0.0446				40
	0.0570 (20 °C)				27
	0.075 (20 °C)				41
	0.041				38
Nonane	0.122	128.26	0.718	151	2
1,1-Dichloroethylene	400.0	96.94	1.218	37	2
Methylene chloride	16300.0	84 93	1.327	40	2
Chloroform	7925.0	119.38	1.483	61.7	2
1,1,2,2-Tetrachloroethane	3100.0	167.85	1 595	146.2	2
	2960				20
1,2-Dichloropropane	2600.0	112.99	1.156	96.4	2
	2420				21

(continued)

TABLE 15 COMPILATION OF AQUEOUS SOLUBILITIES FROM THE LITERATURE FOR ORGANIC COMPOUNDS OF INTEREST TO THE AIR FORCE (concluded)

Compound	Solubility ppm, 25 °C	FW	Density, g/mL	bp, °C	Reference
Dibromochloromethane	NA	208.29	2.451	119	2
1,2,4-Trichlorobenzene	29.8 64 5	181 45	1.454	213	2 21
2,4 Dimethylphenol	NA	122 17	0.965	210	2
1,1,2-Trichlorotrifluoroethane	200.0	187.38	1.579	45 8	2
Methyl ethyl ketone (MEK)	27 5 pph 13.4	72.12	0 805	79 6	2 17
Methyl isobutyl ketone (MIBK)	19100.0 21300.0	100.16	0.80	117	2 22
Methyl cellosolve	Miscible	76.1	0.965	125	2
bis(2-Chloroethyl) ether	NA	143 01	1.220	67	2
Trichlorofluoromethane	1100.0	138 08	1.510	28	2
2,6-Dinitrotoluene	300.0	182.14	1.283	--	2

SECTION V

MIXTURE STUDIES

In this mixture-analysis phase of the work, six components were selected that, theoretically, can interact in multicomponent solutions: benzene, propylbenzene, phenol, 1,2-dichlorobenzene, cis-1,2-dichloroethene, and 1,2-dichloroethane. These chemicals have structural features that can cause either self-association or the formation of molecular complexes. Because halogen substituents are electron-withdrawing, the chlorinated compounds mentioned have induced dipole moments that are attracted to other species with similar partial charges. The propyl substituent in propylbenzene also exhibits electron inductive effects and induced charges. With the "cis" configuration, the chlorinated ethene compound has π-electrons attracted by the chlorine groups to produce a dipole moment. Phenol is known to self-associate by hydrogen bonding in a chain structure, with the length of the chain dependent upon the solution phenol concentration. Another compound in this study that might interact with phenol is bis (2-ethylhexyl) phthalate, but detection limit problems encountered during the single-component runs eliminate it from consideration. Finally, the aromatic compounds may "stack up" in solution because of coordination of the delocalized π-electrons.

The experimental matrix for the mixture runs was designed to acquire qualitative interaction data with a minimum number of EPICS experiments. This is being done with a "T"-test (at the 95 percent confidence level) of the hypothesis that the Henry's law constant in the mixture is the same as the single-component value. Failure of the test indicates the presence of significant chemical interactions in the mixture. The use of several concentration levels demonstrates the concentration dependency of such effects, if they exist. In the mixtures, the concentration of each organic was diluted from its aqueous saturation limit by a factor of six; phenol, however, was also present in one mixture at only 0.5 percent of its saturation limit to investigate composition effects. Serial dilutions of both mixtures are also being run as a further independent check of linear Henry's law equilibrium behavior.

The software necessary to perform the statistical calculations has been written in the form of a Lotus 1-2-3 spreadsheet/macro compatible with other data analysis programs written for this report. The T-test procedure only identifies significant differences in the EPICS average. However, if such differences are found to exist, the binary chemical interactions can be quantified with an appropriate fractional factorial experimental design. Given the low concentrations of interest in this study, the project team originally believed that mixture effects would not be observed and that the "T"-statistic hypothesis test would confirm this. Experimental work in the mixture phase of this investigation, however, suggests the presence of chemical interactions in solution even at low dilutions.

The mixture work has focused on measurements at 20 °C for five different mixtures prepared from the six organic chemicals discussed earlier. The test samples were as follows:

1. Pure components in water

2. Mixture composed of equal volumes of saturated stock solution for each organic

3. Mixture identical to Mixture 2 except that phenol was omitted (a volume of pure water was added to maintain the concentrations of the other chemicals at the same level as Mixture 2)

4. Mixture identical to Mixture 2 except that phenol is present at a much lower concentration (e.g., a concentration of approximately 0.5 percent of the saturation limit)

5. Three-component mixture consisting of benzene, propylbenzene, and 1,2-dichlorobenzene at the same concentration levels as Mixture 2

6. Four-component mixture consisting of benzene, propylbenzene, 1,2-dichlorobenzene, and cis-dichloroethylene at the same concentration levels as in Mixture 2.

Henry's law constants for each component are plotted for these mixtures (along with the single-component results obtained from this study) in Figures 8 through 12. The trends shown in these plots are very interesting because both positive and negative deviations from ideal Henry's law behavior are indicated. Comparing the results for Mixtures 2 and 4, an increasing phenol concentration in multicomponent solution raises the air-water partition coefficient for four of the other components: benzene, propylbenzene, cis-dichloroethylene, and 1,2-dichloroethane. Apparently, strong phenol self-association at higher concentration reduces the affinity of these compounds for the liquid phase. The final chemical, 1,2-dichlorobenzene, did not appear to be affected significantly by changes in the phenol concentration and was therefore, included in all five mixtures as a "benchmark" compound to confirm that the EPICS technique was giving accurate results.

An observed partition coefficient that is lower than the true Henry's law constant represents a negative deviation from ideal behavior. For benzene and propylbenzene, however, positive deviations from ideal solution behavior were also noted during the mixture tests. The partition coefficients measured for these two chemicals in Mixture 3 (no phenol) were significantly higher than the Henry's law constants determined in the single-component measurements, indicating a mixture effect not attributable to the phenol concentration. It appears to be a "salting-out" effect in which one or more of the other organics present in the mixture increase the hydrophobicity of benzene and propylbenzene (e.g., lowers their respective aqueous concentration).

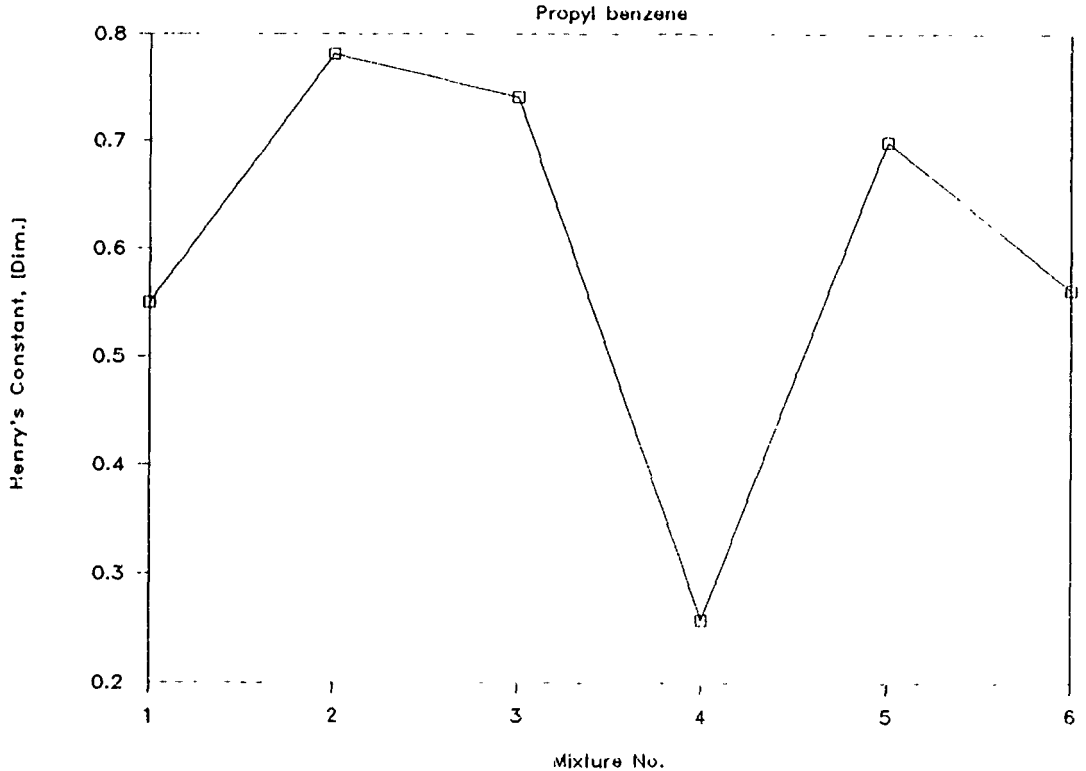

Figure 8. Mixture Study Results for Propyl Benzene.

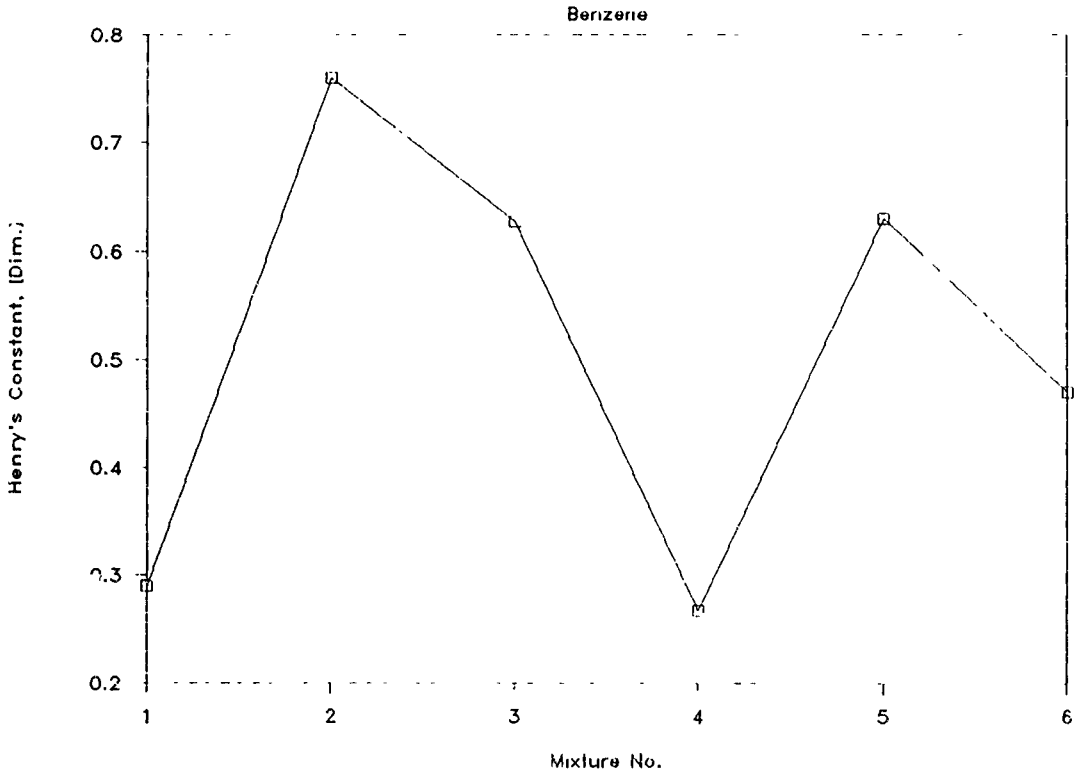

Figure 9. Mixture Study Results for Benzene.

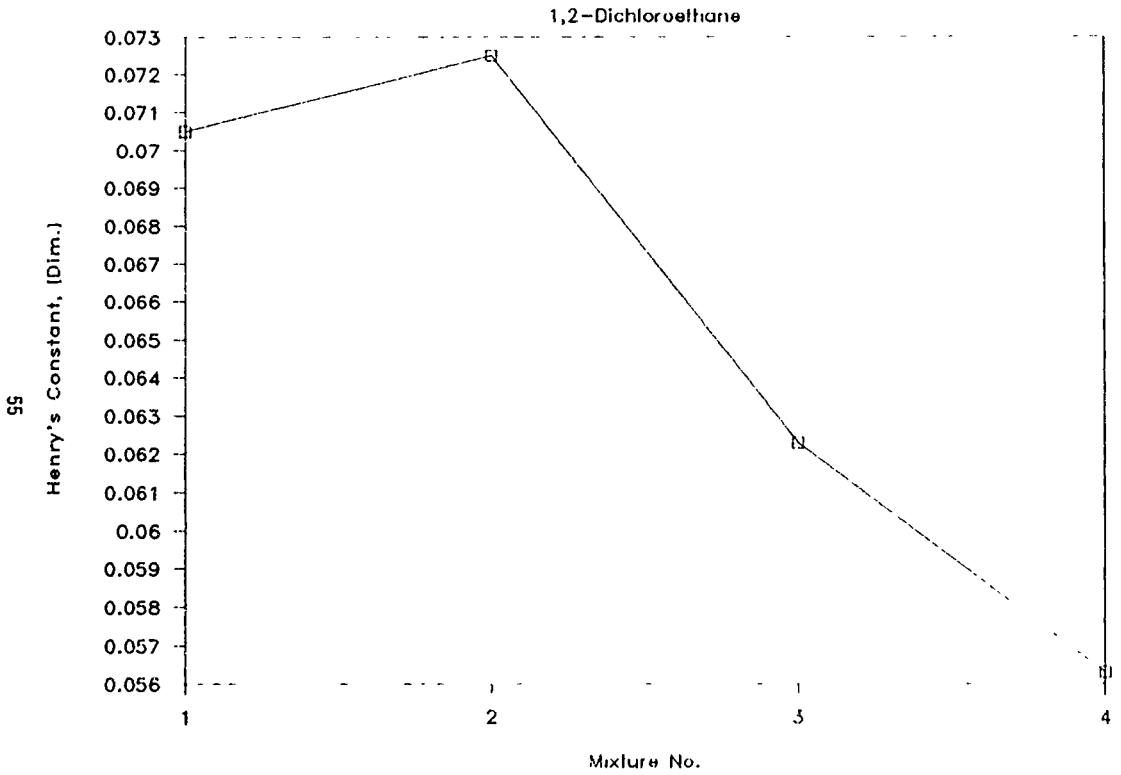

Figure 10. Mixture Study Results for 1,2-Dichloroethane.

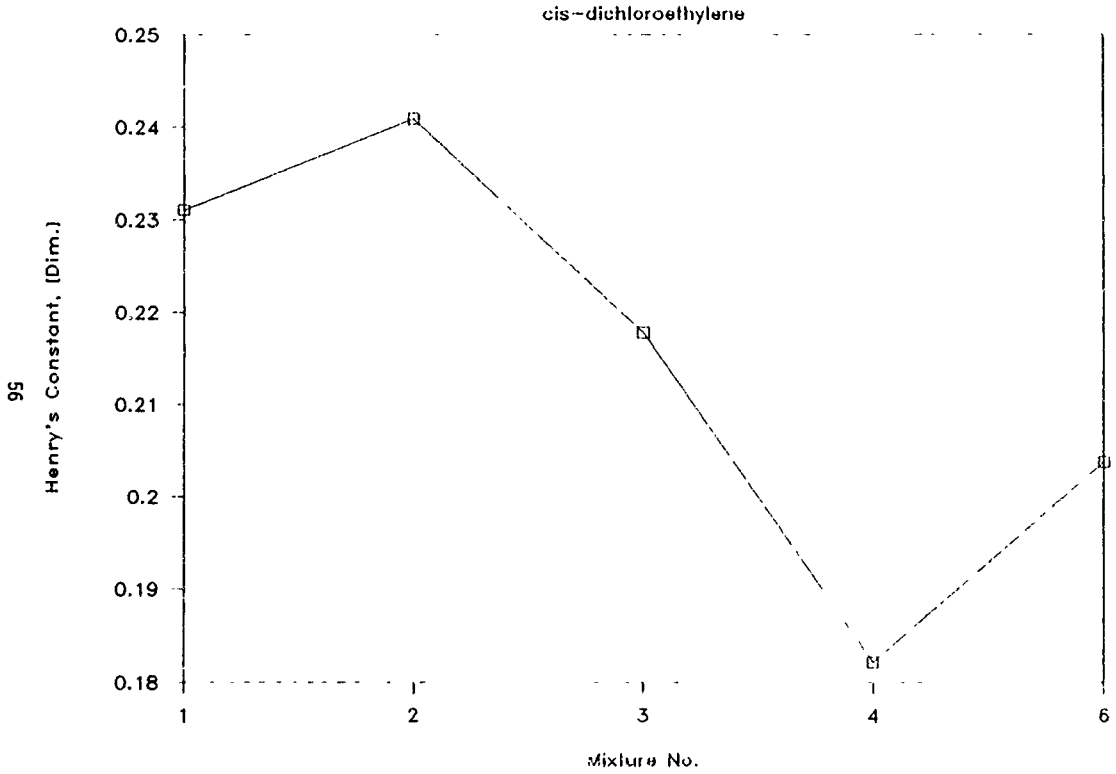

Figure 11. Mixture Study Results for Cis-Dichloroethylene.

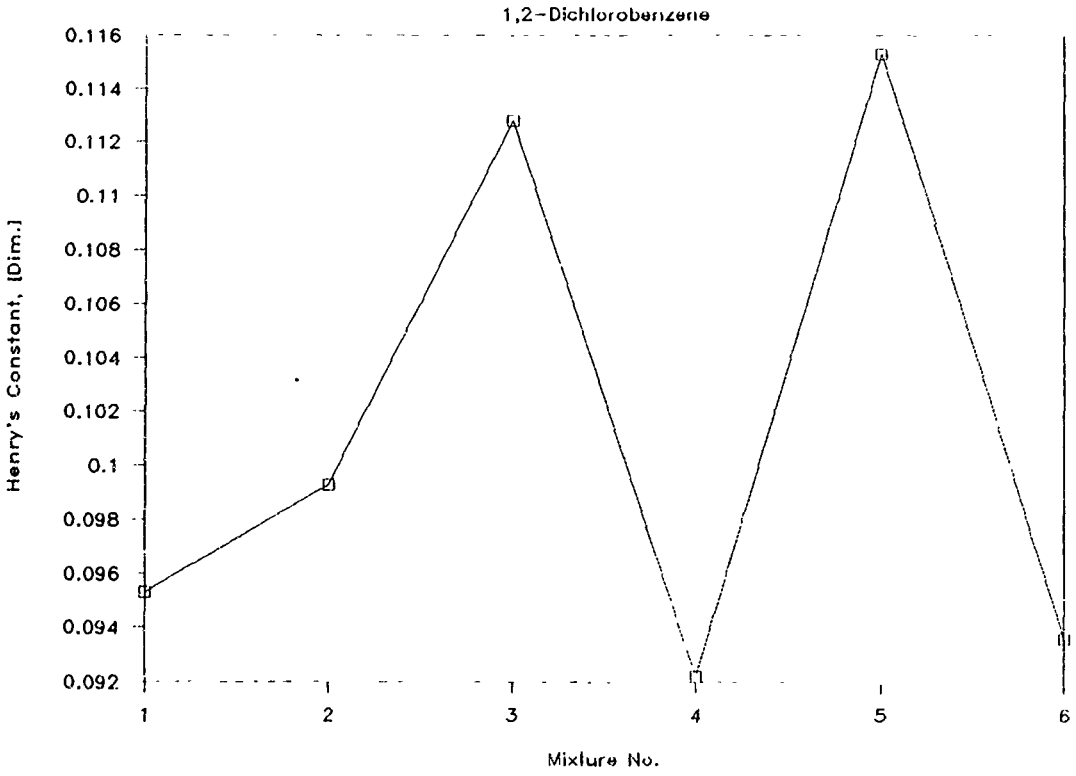

Figure 12. Mixture Study Results for 1,2-Dichlorobenzene.

After observing the above trends, serial dilutions of Mixtures 2, 3, and 4 were analyzed to verify any deviations from ideal Henry's law behavior. Surprisingly, all compounds except phenol were found to have a linear relationship of vapor composition to liquid composition over the entire dilution range. Linear regressions of the mixture serial dilution data resulted in correlation coefficients (r squared values) better than 0.99 for the mixture compounds. Despite the linearity of the dilution curves, the project team believes that the deviations from ideal behavior indicated by the EPICS technique are real and reproducible.

SECTION VI

MODELING

A. COMPUTER DATA ACQUISITION SYSTEM

Extensive computer software was developed to satisfy the data manipulation requirements of the current Henry's law constant measurement program. The EPICS phase of the effort, in particular, has involved extensive "bookkeeping" and data reduction. To address this need, a software package composed of BASIC and LOTUS 1-2-3 programs was written to completely automate the data acquisition process.

The first step in the EPICS data collection procedure is to transmit the integrated peak area from a Hewlett-Packard (HP) 3392A integrator to a personal computer (an IBM-compatible Tandy 1200 HD system) in ASCII format by way of an RS-232C interface. It has also proven desirable to provide the integrator with bookkeeping information from the computer keyboard. This is possible because the HP 3392A, with its own language syntax, can conduct two-way "conversations" with computers by sending and receiving appropriate ASCII character strings. A BASIC program written to operate the asynchronous communication link between the two devices makes use of the HP 3392A language convention for information exchange.

Using this capability, the laboratory analyst designates information, such as a component identifier, the run (bottle) equilibration temperature, the replicate number, etc., that will be inserted onto the printer/plotter copy of the report and permanently stored in a computer report file. The descriptive run information, when cross-referenced against a properly kept laboratory notebook, is an excellent precaution that helps ensure data integrity. Termination of a given run by the analyst at the integrator console causes immediate transmission of the peak area report to the computer. In addition, if a previous report is stored in the integrator memory (active workspace), it may be "customized" and retransmitted.

After the report is stored in a "capture" file by the BASIC program, LOTUS 1-2-3 routines developed specifically for this application are then used to scrutinize the data. The testing order was randomized for statistical validity, but the data manipulation was made more complex. The LOTUS routines are therefore designed to rearrange the data into a logical organizational pattern with descriptive, unique names for the data files.

For instance, one of the LOTUS programs, a "keyboard macro," (in LOTUS terminology) is used to process and organize an entire day's integrator reports. The routine does this by examining a capture file line by line, bracketing each report after detecting the beginning run number and the end-of-report character, and then extracting the pertinent peak areas by position. A

typical capture file contains all runs for 1 day of analysis, with each run consisting of four injections for a single compound at a specified temperature. Each set of extracted component data is given a file name derived from the component identification number, the temperature code, and the replicate number.

Another LOTUS spreadsheet then accesses these individual data files on request and performs the necessary calculations and statistical tests. One such analysis program is created for each component and can be updated as new information is received. Calculated statistical quantities include the coefficient of variation relative standard deviation) for all replicate Henry's law constant observations, the temperature regression parameters (slope and y-intercept) and associated correlation coefficient for each component, and the Student's "T"-test confidence bands for both the raw data and the temperature regression predictions. Using these statistics, it was possible to determine the overall precision of the EPICS procedure for all components and to estimate the accuracy bounds. Appropriate temperature regression and confidence interval plots were generated automatically by the software to present trends graphically. A final LOTUS program was written to combine the data for all of the chemicals into a master tabulated summary convenient to view or manipulate.

Divided according to component, the information generated by the LOTUS software for each chemical is composed of the following:

- Two-page tabulation of the injection peak areas, Henry's law constant estimates, and Coefficient of Variation COV for the component at give temperatures (10, 15, 20, 25, and 30 °C)
- Temperature regression plot (ln H versus 1/T)
- Plot showing the 95 percent confident band on the temperature regression predictions
- Plot illustrating the 95 percent limits (lower and upper) on the averages of the estimates calculated at each temperature.

All of this information is displayed for the 48 compounds of interest in Appendix B of this report.

Similar computer programs have been developed for the bubble column and solubility tests. Again, the emphasis was on ease of data reduction and manipulation, plus valid statistical analyses. In summary, all software items used in the current program allow:

- User-friendly operation
- Simplified data handling/reduction
- Valid statistical tests and
- Elimination of human error.

Because the program functions are completely menu-driven rapid data processing by the laboratory analyst is possible, thereby, providing useful feedback for technique improvement. Most important is the removal of the human element during the data analysis, which has dual benefits of eliminating manual logging errors and ensuring computational accuracy.

B. CORRELATION DEVELOPMENT

To predict the thermophysical properties of VOCs in water a thermodynamic framework for the behavior of pure compounds in water is needed. Three different thermodynamic techniques for correlating experimental Henry's law constants and aqueous solubilities have been examined. Two of these techniques are based on modeling the VOCs as collections of discrete molecular fragments: the UNIQUAC Functional group Activity Coefficient (UNIFAC) model of Fredenslund et al. (Reference 3) and the substituent constant method introduced by Fujita et al. (Reference 42) and described in detail by Leo et al. (Reference 4). The third technique is based on a combined chemical and physical theory of thermodynamic properties, the so-called associated solution theory, as recently applied to Henry's law constant of supercritical gases by Hu et al. (Reference 43). The purpose of using these multiple techniques is to critically evaluate three different, but valid, approaches for their applicability to environmental systems and their predictive capacity for unmeasured multicomponent systems.

1. Unifac Methods

a. Basis of UNIFAC

The UNIFAC model was developed in 1975 to correlate large quantities of data with a few molecular parameters. The first group contribution technique developed for activity coefficient prediction was that of Wilson and Deal (Reference 12); the subsequent development of UNIFAC by Fredenslund et al. (Reference 3) owes much to their early work. Activity coefficients are closely related to various excess properties. In particular, the excess Gibbs' free energy, G^{ex}, may be related to the activity coefficient in a straight forward manner:

$$G_i^{ex} = RT \ln \gamma_i^{**} \quad . \tag{21}$$

In the development of the UNIQUAC equation for phase equilibria Abrams and Prausnitz (Reference 44) used the the concept of local chemical compositions to stipulate that the excess Gibbs' free energy is made up of two parts:

- A contribution due to the difference in volume and surface area of molecules (a configurational part)
- A contribution due to the energetic interactions between molecules (a residual part).

In terms of the activity coefficient, this may be written:

$$\ln\gamma_i = \ln\gamma_i^{\text{configurational}} + \ln\gamma_i^{\text{residual}} \quad . \tag{22}$$

The parameters that appear in UNIFAC are R_k and Q_k, which are van der Waals group volumes and group surface areas, respectively, a molecular coordination number, z; and two binary local composition group interaction parameters, A_{ij} and A_{ji}. The coordination number is arbitrarily set to 10, and then the van der Waals group volumes and group surface areas are obtained directly by rescaling Bondi's (Reference 45) tabulated values. The binary interaction parameters have been obtained for more than 40 different groups by fitting the model to some 55,000 data points, including vapor-liquid equilibria (VLE), liquid-liquid equilibria, infinite dilution activity coefficients and azeotropic points (Reference 13). Of greatest interest to environmentalists may be the recent compilation of infinite dilution activity coefficients (Reference 46) and its application to upgrading the UNIFAC parameters for vapor-liquid equilibria.

Several variations of UNIFAC have been developed recently. The differences in the various models include changes in the combinatorial contribution to the excess free energy, alternate choices for subdividing molecules into groups, the introduction of temperature-dependent parameters, and inclusion of solvation and chemical association effects. The major difficulty in implementing these variants on UNIFAC is the lack of a fitted parameter base. The original UNIFAC model with the latest VLE parameter base was used as the initial benchmark calculation against which to compare our experimental Henry's law constants. The combinatorial contribution to UNIFAC can be modified, as suggested by Kikic et al. (Reference 47). The binary UNIFAC parameters can then be refitted in this same manner to our data base of experimentally obtained infinite dilution activity coefficients. In addition, these group interaction parameters may be fitted to liquid-liquid solubilities of VOCs in water. Then the extent to which optimized parameter values differ between the two data sets can be determined. This modification of UNIFAC offers a potentially more accurate method of predicting Henry's law constants for environmental systems than the original version of UNIFAC.

b. UNIFAC Parameter Fitting

To satisfy the project's thermodynamic modeling objectives, UNIFAC binary interaction parameters were fitted to the experimental VLE (Henry's law constant) data for the aliphatic and aromatic chemicals using a simplex algorithm written for this purpose. A sequential fitting procedure was used rather than simultaneously fitting all the interaction parameters covered by the experimental data. The sequential method required much less computer time, and was judged by the project team to be better suited for updating the correlation database at this time; however, a simultaneous fitting algorithm may be used in the future.

The basic objective was to model the liquid phase activity coefficients of volatile organics infinitely dilute in water using UNIFAC. Then, given experimental Henry's law constants, infinite dilution activity coefficients and optimal binary interaction parameters for UNIFAC were calculated.

A program was written to calculate infinite dilution activity coefficients from experimentally determined Henry's law constants (H_i) for the aliphatic and aromatic chemicals involved in this study. The temperature regression and coefficient of variation results for these compounds were very good, with only a few data points omitted after a visual examination of the data quality. To perform these calculations, pure component vapor pressure data and density data for water at the temperatures of interest were required. A search was conducted for vapor pressure constants for the Antoine Equation and the Harlacher-Braum (HB) equation. Harlacher-Braum constants are scarce, and solution of the H-B equation requires implementation of a Newton-Raphson iteration scheme, initial guesses, etc. Because the Antoine equation predictions are within a few percent of the H-B predictions, the simpler Antoine equation was implemented.

The fugacity coefficient, ϕ, involved in the calculations of γ^{∞}_{VOC} from H_i, was plotted against absolute temperature, T. Over the temperature range 10-30 °C, this quantity was well-approximated by a line, enabling simple linear interpolation of discrete data (see Figure 13). A copy of the FORTRAN code, as well as sample input and output files to perform the calculation of γ^{∞}_{VOC} from H_i may be found in Appendix E (Volume II). The input file SUMMARY.DAT is a file of the experimental Henry's law constants, temperatures, etc. the numbering of which does not exactly correspond to the numbering of the vapor pressure data set (ANTOINE.DAT). The compound list used in the vapor pressure data set is also found in Appendix E. Only the aliphatic and aromatic chemicals in the present work were used in the development of the environmental UNIFAC correlation.

(1) Aliphatics

To test the approach for the data analysis, aliphatic water binary interaction parameters were determined, based on data for 4 compounds: n-nonane, n-hexane, 2-methylpentane, and cyclohexane. Six different objective functions were tested with the optimization routine to determine the best functional form to minimize when fitting interaction parameters. These results are presented in Table 16. The objective function chosen was the relative difference in the natural logarithms of the experimental and calculated activity coefficients. This has a sound theoretical basis, as may be seen from the Gibbs' free energy relationship in Equation (21). The experimental data on which this fit is based, and the comparison of experimental, and predicted infinite dilution activity coefficients (as well as those predicted by the existing VLE database) are shown in Figures 13 through 16. These plots show that the new UNIFAC data base provides a very large improvement in activity coefficient predictions. The improvement demonstrates the merit of this VLE modelling approach.

(2) Aromatics

To optimize the binary interaction parameters associated with aromatic compounds, a much more involved procedure is required. To improve the parameter fit, experimental activity coefficients were plotted against temperature for each compound and obvious outlying points were excluded after

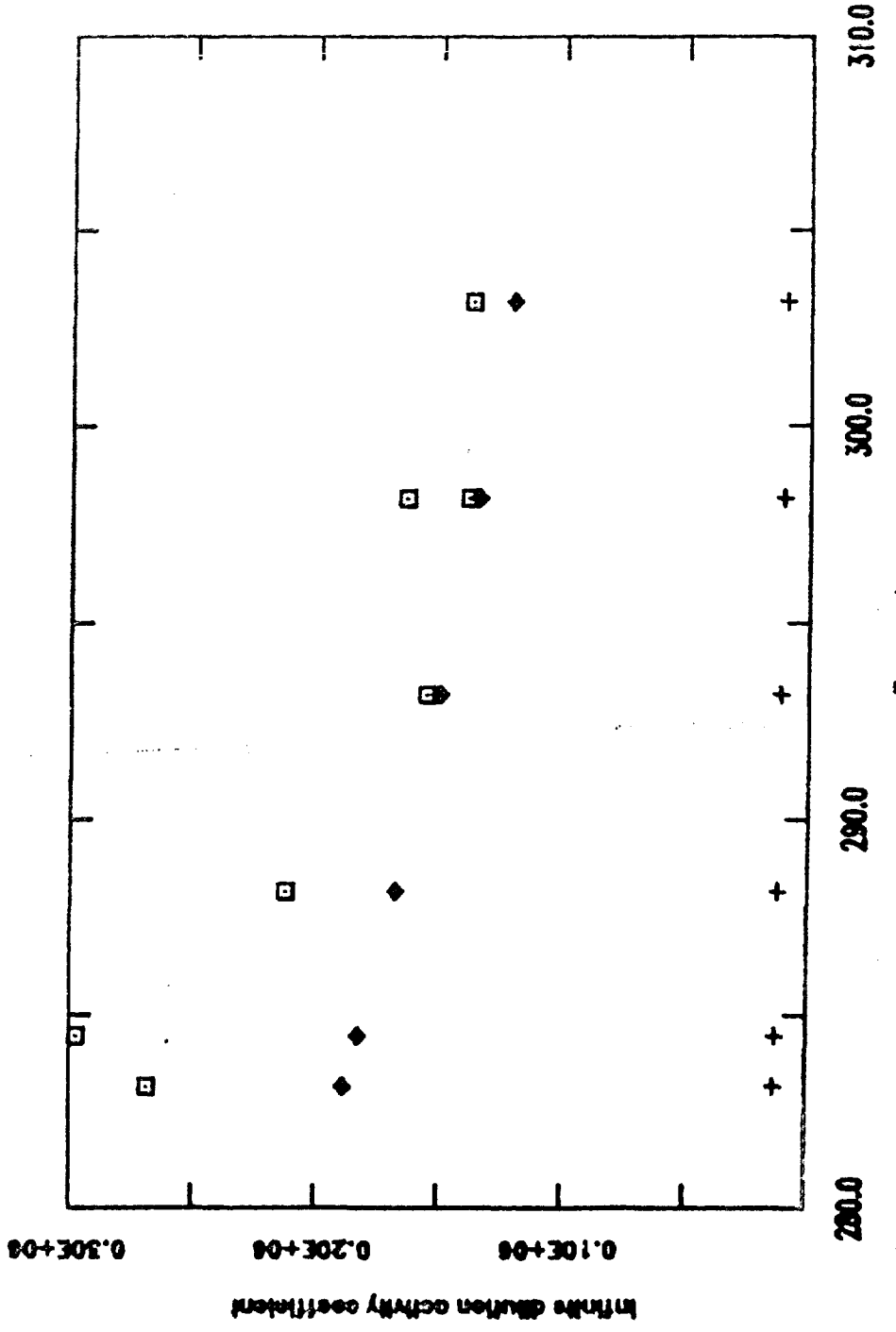

Figure 13. Infinite Dilution Activity Coefficients for 2-Methyl Pentane.
□ - Experimental, + - Old VLE Binary Interaction Parameters,
◇ - New Parameters from This Study.

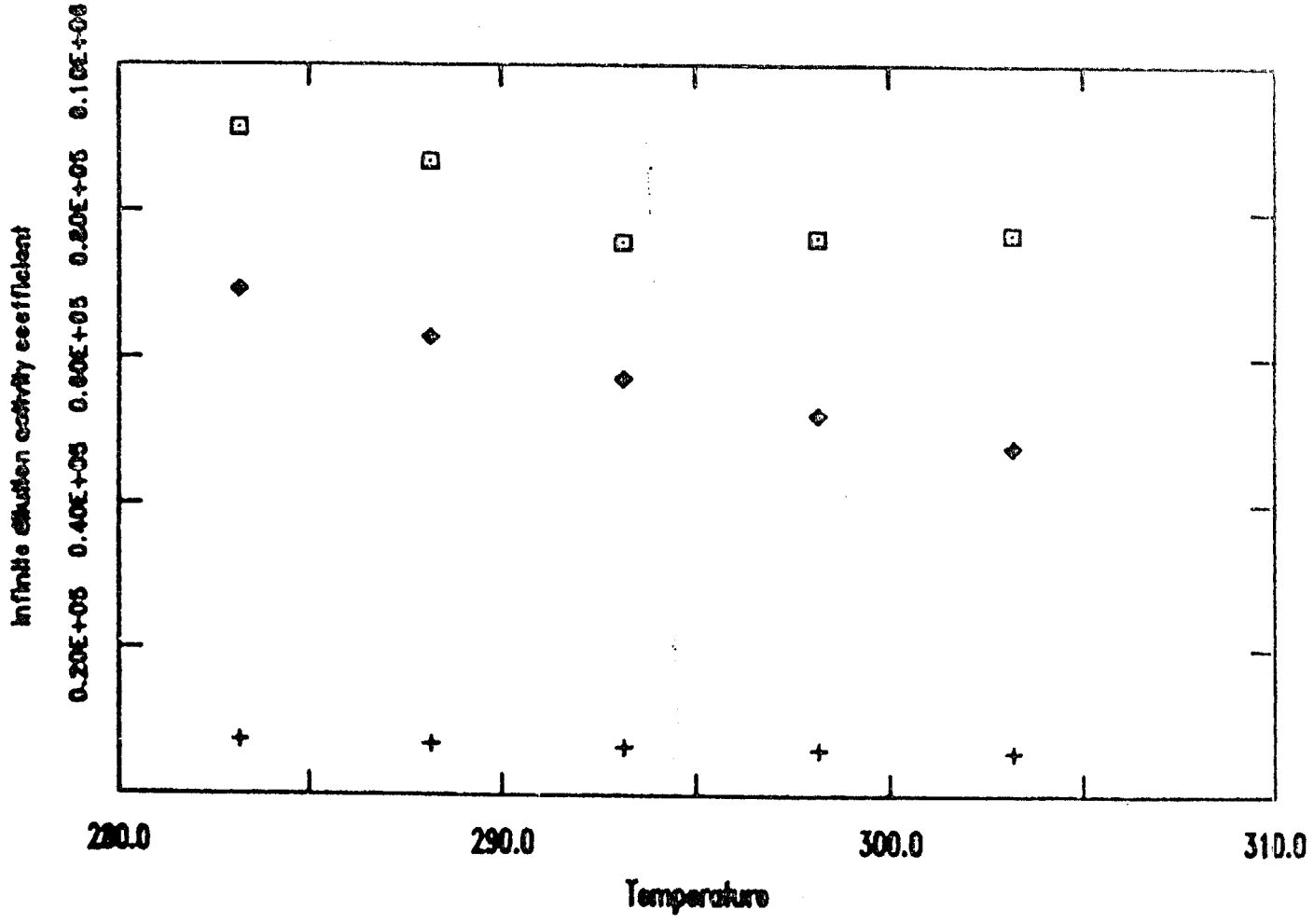

Figure 14. Infinite Dilution Activity Coefficients for Cyclohexane.
□ - Experimental, + - Old VLE Binary Interaction Parameters,
◇ - New Parameters from This Study.

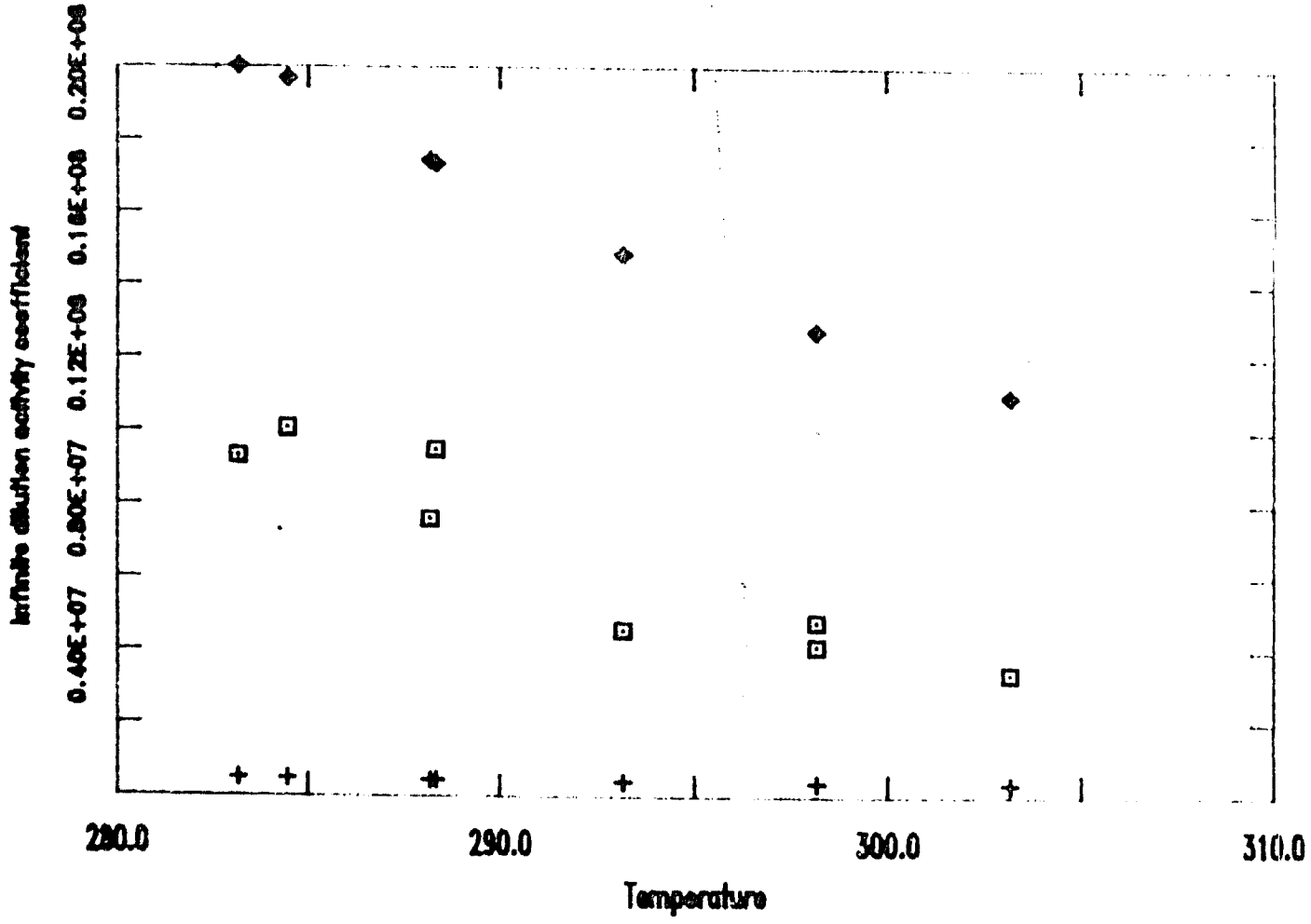

Figure 15. Infinite Dilution Activity Coefficients for n-Nonane.
□ - Experimental, + - Old VLE Binary Interaction Parameters,
◇ - New Parameters from This Study.

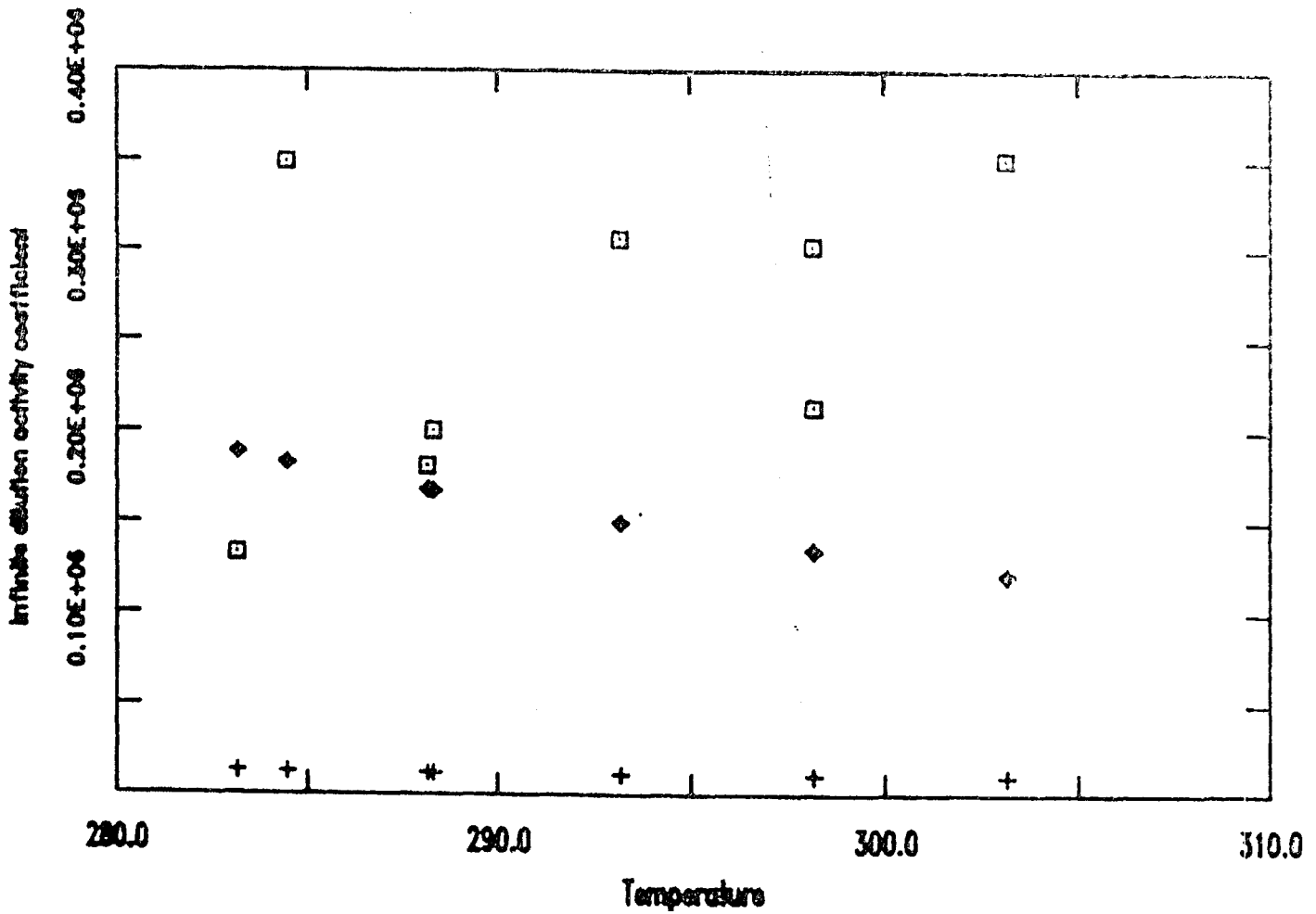

Figure 16. Infinite Dilution Activity Coefficients for n-Hexane.
[ ] - Experimental, + - Old VLE Binary Interaction Parameters,
◇ - New Parameters from This Study.

TABLE 16. LIST OF OBJECTIVE TRIAL FUNCTIONS FOR UNIFAC PARAMETER OPTIMIZATION

Objective function	Binary interaction parameters $A_{H2O-CH3}$	$A_{CH3-H2O}$
Original VLE	300	1318
$(\gamma_{calc} - \gamma_{exptl})^2$ $X_1 = 0$	738	0.0
$(\gamma_{calc} - \gamma_{exptl})^2$ $X_1 = 1$ ppm	738	0.07
$(\ln \gamma_{calc} - \ln \gamma_{exptl})^2$ $X_1 = 1$ ppm	484	5280
$\left(\frac{\gamma_{calc} - \gamma_{exptl}}{\gamma_{exptl}}\right)^2$	745	2.6
$\left(\frac{\ln \gamma_{calc} - \ln \gamma_{exptl}}{\ln \gamma_{calc}}\right)^2$	498	3523
$\left(\frac{\ln \gamma_{calc} - \ln \gamma_{exptl}}{\ln \gamma_{exptl}}\right)^2$ $\gamma_{exptl} = 0.99999$	493	4168

visual inspection. The previously optimized $A_{H2O-CH3}$ interaction parameter was included in the VLE data set. Because γ^{∞} is insensitive to changes in $A_{CH3-H2O}$, it was not modified.

The interaction parameter $A_{H2O-ACH}$ was determined based on the data for benzene only. This value was substituted into the VLE data set, and the new interaction parameters – $A_{H2O-ACCH}$, $A_{ACH-ACCH3}$, and $A_{ACCH3-ACH}$ – were then determined based on data for ortho, meta, and para-xylene; trimethylbenzene; and toluene. The VLE data set was again updated to reflect changes in these parameters. To continue the sequence, a new value of $A_{H2O-ACH}$ was determined based on the data for benzene, the xylenes, trimethyl benzene, and toluene, and database again updated. Finally, new values for the interaction

parameters - $A_{H2O-ACCH3}$, $A_{ACH-ACCH3}$, and $A_{ACCH3-ACH}$ were determined from the revised data.

This sequence of updating and refitting continues iteratively until the the numerical values of each of the five interaction parameters converges to a constant value. From trial runs, this solution does indeed appear to be converging with each iteration. Results from this procedure are shown in Table 17. The next portion of the overall modeling effort would be to increase the scope of this iteration series to include alkyl-substituted aromatics (e.g., methyl ethylbenzene), and, finally, the halogenated compounds. Unfortunately, this expanded fitting scheme was beyond the scope of the current work.

TABLE 17. FITTING PROCEDURE FOR BINARY INTERACTION PARAMETERS

$A_{H2O-CH3}$ = 492.6 (from optimization of aliphatic hydrocarbon/water data)		
Original VLE data base	Iteration 1	Iteration 2
$A_{H2O-ACH}$ = 362.3	533.218 (based on benzene)	443.966
$A_{H2O-ACCH3}$ = 377.6	133.554	214.480
$A_{ACH-ACCH3}$ = 167.0	-300.469	-604.445
$A_{ACCH3-ACH}$ = -146.8	278.024	447.705

2. Group Contribution Method

The second thermodynamic technique investigated for correlating Henry's law constants of VOCs in water is the simple substituent constant method of Leo et al. (Reference 4). By analogy with the Hammett constant technique from physical organic chemistry, Fujita, et al. (Reference 42) developed a substituent constant approach for computing Henry's law constants and octanol-water partition coefficients, which relies on the additivity of the free energetic contributions to both properties. This technique is described in full in Leo et al. (Reference 4) and has some potential advantages over the UNIFAC method. Despite its strictly correlational approach, it can in principal account for inductive, resonant, steric, branching, and conformational effects that are completely ignored by the UNIFAC model.

The correlation of equilibrium air-water partition coefficients with molecular structure is a formidable task due to the difficulty in isolating the competing functional group influences. Attempts to predict partition coefficients using a group contribution approach have proven successful when the reference system(s) have been chosen so that similar steric and electronic

interactions are present in the derivative compounds. The additivity constant (π) for a given substituent group (designated by "X") is defined by Leo et al. (Reference 4) as follows:

$$\pi_X = \log_{10} P_X - \log_{10} P_H \tag{23}$$

where

P_X = partition coefficient of the derivative compound

P_H = partition coefficient of the parent molecule

π_X = logarithm of the partition coefficient for the function X.

Summing the appropriate π_X values for the various functional group and structural elements of a compound of interest gives the logarithm of its predicted partition coefficient.

Values of π correlated for a substituted species in a homologous series have been shown by Leo et al. (Reference 4) to be relatively constant for the octanol-water system. For example, the addition of methyl groups to various benzene derivatives has been found to yield π-$_{CH3}$ values, which are surprisingly constant at around 0.5.

There is thermodynamic justification for assuming that Henry's law constant may obey the form of Equation (23), if one considers Henry's law constant to be analogous to an equilibrium constant. Letting N denote the parent molecule and X the fragment of interest, the following reactions describe the phase equilibria between air and water for the parent and its derivative:

$$\text{PARENT} \quad (N\text{-}H)_{H_2O} \overset{K_1}{\rightleftharpoons} (N\text{-}H)_{air}, \quad K_1 = \frac{[(N\text{-}H)_{air}]}{[(N\text{-}H)_{H_2O}]} \tag{24}$$

$$\text{DERIVATIVE} \quad (N\text{-}X)_{H_2O} \overset{K_2}{\rightleftharpoons} (N\text{-}H)_{air}, \quad K_2 = \frac{[(N\text{-}X)_{air}]}{[(N\text{-}X)H_2O]} \tag{25}$$

where

K_i = equilibrium constant

[] = species concentration.

The quantity π_X, from the form of Equation (23), is therefore

$$\pi = \log_{10} \left[\frac{K_2}{K_1}\right] \tag{26}$$

with (K_2/K_1) being the equilibrium constant for the overall reaction:

$$(N\text{-}X)_{H_2O} + (N\text{-}H)_{air} \rightleftarrows (N\text{-}X)_{air} + (N\text{-}H)_{H_2O} \quad . \tag{27}$$

The free energy change resulting from the introduction of the substituent X is obtained from this reaction as follows:

$$\Delta G_{total} = 2.303\ RT\ \log_{10}\left(K_2/K_1\right) = G^{air}_{(N\text{-}X)} + G^{H_2O}_{(N\text{-}H)} - G^{H_2O}_{(N\text{-}X)} + G^{air}_{(N\text{-}H)} \quad . \tag{28}$$

The assumption that the free energy of an individual molecule can be represented as the sum of the free energies of its part plus their interactions gives rise to the expressions:

$$G_{(N\text{-}H)} = G_N + G_H + G_{NH} \tag{29}$$

and

$$G_{(N\text{-}X)} = G_N + G_X + G_{NX} \quad .$$

Putting these equations into Equation (15) gives the result:

$$2.303\ RT\ \log_{10}\ (K_2/K_1) = \Delta G_X + \Delta G_{NX} - \Delta G_{NH} - \Delta G_H \tag{30}$$

where

$$\Delta G_i = G_i^{air} - G_i^{H_2O} \quad . \tag{31}$$

If the interaction terms may be neglected, we get the following expression for π_X:

$$2.303\ RT\ \log_{10}\ (K_2/K_1) = \Delta G_X - \Delta G_H \tag{32}$$

or

$$\pi_X = \log_{10}(K_2/K_1) = \frac{\Delta G_X - \Delta G_H}{2.303\ RT} \quad . \tag{33}$$

The definition of π_X, as shown here, is physically defensible because it is related to the free energy change in a partitioned compound that results when a substituent X replaces a hydrogen atom of the parent compound.

3. Intramolecular Influences on Partitioning

For development of a comprehensive fragment correlation, it is necessary to isolate and quantify at least five different types of functional group effects on Henry's law constant:

- Inductive effects
- Effects of resonance
- Steric effects
- Effects of branching
- Conformational effects and "rigidity."

The following paragraphs discuss these structural influences and give qualitative examples of their relationship to partitioning behavior.

a. Inductive Effects

Inductive effects are the result of electron-withdrawing substituents that make the lone-pair electrons belonging to a second functional group (such as OH) less available for hydrogen bonding. This decreases the affinity of the compound for the water phase, thus, raising the value of Henry's law constant. A group contribution correlation can account for this behavior by including π values for the addition of electron-withdrawing groups (such as NO_2) to parent compounds containing functional groups with electrons available for hydrogen bonding.

b. Effects of Resonance

The effect of electron delocalization on π values should also be included in a group contribution correlation. For octanol-water systems, the partition coefficient increases as the result of transferring a functional group from an aliphatic to an aromatic position. Similar behavior may also be anticipated for Henry's law constant. Another electronic effect worth studying is the presence of multiple bonds (double, triple) as well as conjugated double bonds.

c. Steric Effects

Steric effects are quite varied in nature, with the most common perhaps being a case in which the Henry's law constant increases because lone-pair electrons (on an OH group, for instance) are shielded from the surrounding water molecules. This blocking of a hydrophylic functional group could be the result of inert alkyl groups, crowding of functional groups, or chain branching. Intuitively, one would expect that all such circumstances would decrease the hydrogen bonding capability of the compound.

d. Effects of Branching

Branching is another important factor in correlating Henry's law constant with chemical structure. Work with the octanol-water system has already shown (Reference 4) that branching results in lower substituent π values than for a "normal" configuration when aliphatic compounds are considered. Furthermore, when branching in that chemical class occurs at the

functional group, the effect appears to be slightly greater, with the contrast between the normal and "branched" configurations becoming more evident. Because of uncertainties in this area, however, a constant value of π for the effect of branching on the octanol-water partition coefficient has been chosen (Reference 4), and it may prove desirable to take the same approach for Henry's law constant.

e. Conformational Effects

Conformational effects are closely related to rigidity and both should be considered in a structural correlation. For example, a simple case of conformational influences occurs when long aliphatic chains tend to coil up on solution, forming molecular oil droplets. Another very interesting example occurs in certain phenyl derivatives when the dipole of a side chain interacts with the delocalized electrons of the ring. This causes "folding" of the side chain onto the phenyl ring that promotes intramolecular hydrogen bonding. Presumably, such attractions would tend to give the compound an aqueous solubility greater than expected, thus, lowering the anticipated Henry's law constant.

f. Rigidity Effects

The effect of the rigidity of a molecule on the logarithm of its Henry's law constant (a quantity analogous to lipophilicity) may also be important. Because the Henry's law constant of a compound will be calculated from small, flexible fragments, restricted rotation in the compound may have an adverse effect on the accuracy of the correlation. Based on the ideas of Aranow and Witten (Reference 48), rigid molecules should have a lower experimental Henry's law constant than that predicted by such a correlation. This suggests two conclusions:

- A "rigidity factor" should be included in a predictive correlation.
- Such a factor would be entropy related and, thus, temperature dependent.

The second conclusion implies that if the rigidity changes significantly in a homologous series of compounds, the effect on the temperature dependency of the structural contributions to Henry's law constant could be significant.

4. Other Approaches

The final thermodynamic technique evaluated in this study is the associated solution theory. Originally developed as a purely chemical theory of nonidealities by Dolezelak in 1908, (Reference 49), the method has been recently combined with physical theories of nonidealities to generate models of Henry's law constants in water (Reference 43). The model is based on a four-step calculation of the free energy of dissolving a gaseous component in water: (1) formation of pure associated and solvated species in the perfect gas state, (2) mixing of the pure associated and solvated species in the

perfect gas state, (3) introducing a hard-sphere contribution to the energy, and (4) imposing an unattractive potential on the hard-sphere mixture of associated and solvated species. The model has proven successful in correlating Henry's law constants of pentane, hexane, and benzene in water at temperatures from 0 to 300 °C. Future correlation work may include testing the model against the existing environmental data base and extending it to mixtures for comparison with the modified UNIFAC method and the Hansch substituent group method.

C. COMPUTER SOFTWARE

The UNIFAC algorithm has been implemented as a FORTRAN computer program that can be run on any IBM-compatible (MS-DOS) personal computer. With this software, Henry's law constants and aqueous solubilities can be calculated for "new" compounds (i.e., those not represented in the current VLE database) from their constituent structural groups. Partition coefficients for organic compounds in multicomponent mixtures can also be calculated with the UNIFAC software. The simplex algorithm for fitting binary interaction parameters to experimental data in the manner explained above is included in the software package to give the Air Force the ability to update the UNIFAC database with future in-house measurements. At present, this computer simplex routine is in "batch" form (i.e., input/output operations are not interactive).

To make the VLE and LLE algorithms easy to use, the FORTRAN routines are written in modular form, and the modules connected by interactive menus and graphics screens. All graphics are produced using Turbo Pascal, a procedure-oriented computer language. In their present form, the software menus are programmed primarily at the DOS level, thereby, making program modifications easier. The interactive FORTRAN programs automatically prompt the user for data input (on the screen) when necessary, and output is sent both to the screen and to a disk file that can be readily printed.

1. Binary Interaction Databases

A "demonstration" diskette containing the UNIFAC algorithms has been developed to illustrate the potential of the UNIFAC fragment approach for calculating Henry's Constants and aqueous solubilities. The chemical fragment tables (Tables 18 and 19) accompanying this report should be utilized when running the UNIFAC programs. The most recently published VLE and LLE databases are integrated into the software, and either database can be interactively selected by the user from the screen. UNIFAC binary interaction parameters determined from the experimental Henry's law constant data have also been added to the original VLE parameters to give a third "environmental" (infinite dilution) database. The user, therefore, has three database choices onscreen when running the UNIFAC software.

Note from Tables 18 and 19 that the main group and subgroup identification numbers for a given fragment differ between the VLE and LLE databases. (Subgroup identification numbers for the environmental database are identical to those used in the VLE database.) The database selected should, therefore, be kept in mind when entering group identification numbers. In

TABLE 18. SUBGROUP ID NUMBERS FOR VLE DATA BASE

DATABASE OF UNIFAC VLE-PARAMETERS

Group designations of Gmehling, Rasmussen, and Fredenslund, (1982)

••• VAPOR-LIQUID EQULIBRIUM •••

THE MAIN GROUPS ARE:

1) CH2	2) C=C	3) ACH	4) ACCH2	5) OH .....
6) CH3OH	7) H2O	8) ACOH	9) CH2CO ...	10) CHO .....
11) CCOO	12) HCOO	13) CH2O	14) CNH2	15) CNH .....
16) (C)3N	17) ACNH2 ...	18) PYRIDINE	19) CCN	20) COOH .....
21) CCL	22) CCL2 .. .	23) CCL3	24) CCL4	25) ACCL .....
26) CNO2	27) ACNO2 ...	28) CS2	29) CH3SH ...	30) FURFURAL .
31) DOH	32) I	33) BR	34) C=-C	35) DMSO .....
36) ACRY	37) CLCC	38) ACF	39) DMF	40) CF2 .....

THE SUB GROUPS ARE:

1) CH3	2) CH2	3) CH	4) C	5) CH2=CH ...
6) CH=CH	7) CH2=C	8) CH=C	9) C=C	10) ACH .....
11) AC	12) ACCH3 ...	13) ACCH2 ...	14) ACCH	15) OH .....
16) CH3OH	17) H2O	18) ACOH	19) CH3CO ...	20) CH2CO ....
21) CHO	22) CH3COO ..	23) CH2COO ..	24) HCOO	25) CH3O .....
26) CH2O	27) CH-O	28) FCH2O ...	29) CH3NH2 ..	30) CH2NH2 ...
31) CHNH2	32) CH3NH ...	33) CH2NH ...	34) CHNH	35) CH3N .....
36) CH2N	37) ACNH2 ...	38) C5H5N ...	39) C5H4N ...	40) C5H3N ....
41) CH3CN	42) CH2CN ...	43) COOH	44) HCOOH ...	45) CH2CL ....
46) CHCL	47) CCL	48) CH2CL2 ..	49) CHCL2 ...	50) CCL2 .....
51) CHCL3	52) CCL3	53) CCL4	54) ACCL	55) CH3NO2 ...
56) CH2NO2 ...	57) CHNO2 ...	58) ACNO2 ...	59) CS2	60) CH3SH ....
61) CH2SH	62) FURFURAL	63) (CH2OH)2	64) I	65) BR .....
66) CH=-C	67) C=-C	68) DMSO	69) ACRY	70) CL(C=-C) .
71) ACF	72) DMF-1 ...	73) DMF-2 ...	74) CFS	75) CF2 .....
76) CF				

TABLE 19. SUBGROUP ID NUMBERS FOR LLE DATA BASE

DATABASE OF UNIFAC LLE-PARAMETERS

Group designations of Magnussen, Rasmussen, and Fredenslund, (1981)

••• LIQUID-LIQUID EQULIBRIUM •••

THE MAIN GROUPS ARE:

1) CH2	2) C=C	3) ACH	4) ACCH2	5) OH .....
6) P1	7) P2	8) H2O	9) ACOH	10) CH2CO ....
11) CHO	12) FURFURAL	13) COOH	14) COOC	15) CH2O .....
16) CCL	17) CCL2	18) CCL3	19) CCL4	20) ACCL .....
21) CCN	22) ACNH2 ...	23) CNO2	24) ACNO2 ...	25) DOH .....
26) DEOH	27) PYRIDINE	28) TCE	29) MFA	30) DMFA .....
31) TMS	32) DMSO			

THE SUB GROUPS ARE:

1) CH3	2) CH2	3) CH	4) C	5) CH2=CH ...
6) CH=CH	7) CH=C	8) CH2=C	9) ACH	10) AC .....
11) ACCH3	12) ACCH2 ...	13) ACCH ...	14) OH	15) P1 .....
16) P2	17) H2O	18) ACOH	19) CH3CO ...	20) CH2CO ....
21) CHO	22) FURFURAL	23) COOH	24) HCOOH ...	25) CH3COO ...
26) CH2COO ...	27) CH3O	28) CH2O	29) CH-O	30) FCH2O ....
31) CH2CL	32) CHCL	33) CCL	34) CH2CL2 ..	35) CHCL2 ....
36) CCL2	37) CHCL3 ...	38) CCL3	39) CCL4	40) ACCL .....
41) CH3CN	42) CH2CN ...	43) ACNH2 ...	44) CH3NO2 ..	45) CH2NO2 ...
46) CHNO2	47) ACNO2 ...	48) (CH2OH)2	49) (HOMM)2O	50) C5H5N ....
51) C5H4N	52) C5H3N ...	53) CCL2=CHCL	54) HCONHCH3	55) HCON(CH3)2
56) (CH2)4SO2	57) (CH2)2SO			

addition, enter only subgroup numbers (not main group numbers) and construct the chemical(s) of interest from the appropriate subgroup table.

The benzene/water system is an excellent test case for two reasons: (1) that system's well-known experimental results, and (2) the simplicity of subdividing these chemicals into subgroups. For example, benzene is composed merely of six aromatic carbon-hydrogen subgroups ("ACH"), and water is a single subgroup ("H_2O"). Several such test cases have been run to debug and validate the UNIFAC software.

2. Documentation for the Simplex Fitting Program

As described earlier, two FORTRAN programs were written to implement the three fragment databases: a simplex fitting algorithm and an interactive, menu-driven program to calculate Henry's law constants and aqueous solubilities. The latter program can also determine how a volatile chemical in a multicomponent liquid solution will partition between the vapor and the liquid phases at equilibrium. Mixture effects on equilibrium behavior can, thus, be quantified and predicted.

The above software items were designed for ease of use. The simplex routine was written to fit UNIFAC binary interaction parameters to the experimental Henry's law constant data collected over the course of this study. For the sake of simplicity, this program is in "batch" form (i.e., all input operations involve reading from ASCII data files) and is not interactive. The simplex software is a modification of a routine published by Fredenslund et al. (Reference 3); the interested reader should refer to their discussion of the theory behind the simplex algorithm. In the procedure for running the simplex program, the user supplies only two things: (1) the subgroup breakdown (i.e., the number of each type of subgroup) for each chemical of interest, and (2) the experimental activity coefficient data for the pertinent binary system. Up to four binary interaction parameters can be fitted simultaneously with the current software configuration. Typically, these would be the interaction parameters $A_{i,j}$ and $A_{j,i}$ for groups "i" and "j," plus a second pair, $A_{k,l}$ and $A_{l,k}$, for two additional subgroups. Note that $A_{i,j}$ and $A_{j,i}$ are not, in general, numerically equivalent.

As an example of the fitting procedure, consider the determination of the binary parameters for two subgroups: ACH and H2O. The necessary binary experimental data could come from any of a number of systems containing the subgroups of interest, such as benzene/water, toluene/water, or xylene/water. There are a total of three main groups in these binary systems: (1) ACH...(ACH subgroup), (2) AC-CH2... (AC-CH3 subgroup), and (3) H2O... (H2O subgroup). Because a main group's interaction with itself is defined to be zero, a total of six interaction parameters must either be fitted or supplied by the user. The toluene/water system, for instance, has every one of the six (6) possible binary interaction pairs:

- ACH and AC-CH3,
- AC-CH3 and ACH,

- ACH and H2O,
- H2O and ACH,
- AC-CH3 and H2O,
- H2O and AC-CH3.

As further illustration, the simplex algorithm could simultaneously fit interaction parameters 3-6 above, but values for Parameter 1 and 2 are needed to complete the structural description of both toluene and xylene. Parameters 1 and 2 would either be estimated, supplied from a previous simplex fitting run, or taken from the published VLE database of Gmehling, Rasmussen, and Fredenslund (Reference 9). Clearly, when multiple compounds and subgroups are considered, the fitting procedure becomes very complex. In the present work, a sequential fit (i.e, using previously fitted interaction pairs to aid in fitting subsequent pairs) was selected to minimize computer time. Perhaps a more desirable future approach would be to fit all interaction parameters simultaneously with a pattern search algorithm (e.g., Hooke-Jeeves) to minimize the difference between the experimental and calculated activity coefficients.

3. Documentation for the Interactive UNIFAC Program

The interactive UNIFAC program to calculate Henry's law constant and aqueous solubility is very simple to operate. It can be run on any IBM-compatible personal computer that supports the MS-DOS or PC-DOS operating systems and may be installed on a hard disk if desired. To run the program from a floppy disk, the following steps should be performed:

- Insert the program disk into the designated drive and change the screen drive prompt to the appropriate letter (e.g., "A>").
- Type the command "UNIFAC" at the DOS drive prompt and press [Enter] to invoke the program.
- A graphics start-up screen will apoear while the program initializes, after which a selection menu will appear.
- Select "A" for calculation of Henry's Constant, "B" for the simplex routine (not installed in the current version), and "C" for the liquid-liquid flash algorithm (e.g.. an iterative Newton-Raphson procedure) to calculate aqueous solubility.
- Follow all instructions as they are displayed onscreen and supply information from the keyboard as requested. Program output is written both to the console (screen) and to a disk ASCII file that can be routed to virtually any printer or imported into Lotus 1-2-3 and most other commercial programs. Printing the program output can be done with the following DOS copy command: "copy UNIFAC.OUT lpt1:." This assumes connection of the printer to parallel port 1.

but other printer interfaces (e.g., lpt2:, com1:, and com2:) can also be used.

- After calculations are terminated and the results displayed, the program queries the user whether to return to the Main Menu or continue. This feature allows the user to re-run a branch of the program multiple times without having to return to the Main Menu after each pass.

- At the Main Menu, the user has the option of selecting another item or exiting the program by pressing the [Escape] key. Leaving the program returns the user to the initial DOS drive prompt.

To operate the program from a hard disk instead of a floppy disk, simply create a hard disk directory (at the "C>" prompt) with the DOS command "md c:\UNIFAC." Then place the original program diskette into drive A and enter the following DOS command at the "C>" prompt: "copy a:*.* c:\UNIFAC." To run the program, simply enter the DOS command "cd \UNIFAC" at the "C>" prompt and type "UNIFAC." The program should then run normally according to the above instructions for floppy disk operation. When duplicating the original program diskette, always copy the contents of the entire diskette since the UNIFAC program uses all the files and expects to find them in the startup directory. Because the original UNIFAC diskette contains the MS-DOS 2.11 operating system, it is recommended that the "diskcopy" commands be used to exactly duplicate the UNIFAC disk. The original program diskette will then "boot" the system. That is, if the disk is placed in drive A: and the computer turned on, the UNIFAC program will come up without any further commands. For users with limited computer experience, this may be the preferred call-up procedure.

The only data necessary to run the interactive program are the subgroup ID numbers (see Table 18 or 19) that describe the chemicals of interest, the absolute temperature of the system, and pure component vapor pressure data if Henry's law constants are to be calculated. Antoine coefficients can also be supplied instead of component vapor pressures if they are available.

SECTION VII

CONCLUSIONS

Experimentally determined Henry's law constants from this study agreed well with other reported values. However, for many of the compounds there were very few, if any, experimentally determined values with which to compare, and rarely were the results presented with confirming statistics. In many cases, agreement between experimentally determined Henry's law constants and values estimated using the ratio of vapor pressure and aqueous solubility was quite good. However, depending on the application of the data (i.e., required accuracy) care should be exercised when using estimated values, as differences of over 400 percent were noted. Equilibrium Partitioning in Closed Systems (EPICS) is an attractive methodology for directly determining these partitioning values. This simple technique employs standard gas chromatography headspace analysis, and absolute gas phase concentrations are not needed for the analysis. The EPICS headspace method is applicable over a wide volatility range and exhibits excellent precision and reproducibility from one laboratory to another. Batch air stripping is comparable in accuracy to EPICS for dilute aqueous solutions of less volatile compounds. However, long bubble retention times may be required to achieve gas-liquid equilibrium for volatile constituents, and axial concentration gradients may arise when tall columns or low gas flow rates are employed.

Mixtures of different contaminants may cause both positive and negative deviations from ideal solution behavior due to intermolecular effects such as association and solvation. These systems of mixtures more closely resemble actual environmental contamination problems than do neat single component solutions. The EPICS technique allows ready analysis of the apparent Henry's law constant of each component in these mixtures. This information would permit the more reliable design of treatment facilities for contaminated groundwater or other waste matrices; however, meaningful interpretation of these results awaits the development of a predictive multicomponent model.

The shake-flask method proved to be the most reliable technique for determining aqueous solubilities of the three methods employed. Local maxima and minima of solubility with respect to temperature were observed, but often these extremes were not statistically significant. The correlation of the solubility data to the Henry's law constant results is not possible at this time.

The UNIFAC method has proven to be the most effective way of utilizing the current VLE data in a general thermodynamic correlation of aqueous solubilities and Henry's law constants. A computer algorithm to fit the current data to a new environmental UNIFAC binary interaction database has been developed, and a portion of the experimental data collected incorporated into this new database. The new database creates a considerable improvement in the predictions generated by UNIFAC in the dilute concentration regime (Figures 13 through 16). Additional effort will be required to completely fit the current experimental data with the environmental UNIFAC database.

SECTION VIII

RECOMMENDATIONS

Based on the encouraging results of this study, there are opportunities for future work in several areas: (1) extension and refinement of the binary interaction fitting procedure begun in this study, (2) continued development of interactive software to implement the UNIFAC concept, and (3) additional experimental measurements. Continued work in all three areas is essential to achieving the goal of a comprehensive UNIFAC "environmental" database that is easy to use.

A. CORRELATION DEVELOPMENT

Further work in fitting UNIFAC binary interaction parameters would be greatly aided by the following actions:

- Extension of the simplex program to handle the simultaneous fitting of more than the current two pairs of interaction parameters
- Modification of the simplex program to eliminate forced optimization in pairs, especially if the water-subgroup interaction parameter (e.g., $A_{H2O-***}$) is assumed to be invariant
- Rewrite the simplex program's input-output statements to eliminate the necessity of entering water mole fractions and experimental activity coefficients since these are the same in all cases
- Change the output file format for the interactive Henry's law program to match the necessary input file format for the simplex program, and perhaps make this common format compatible with a standard plot routine.

Computer software development is an essential part of implementing the UNIFAC algorithm in a manner that meets Air Force needs. The software package developed under the current contract can be improved in several specific ways. One area of future attention would be better screen cursor positioning and data input. For instance, the program now prompts the user sequentially for subgroup identification numbers and does not allow an entered value to be changed. A better approach would be to have full-screen input of data by columns.

Applied to Subgroup ID inputs, this would involve displaying the available subgroups on the screen in several parallel columns with a highlighted cursor-

arrow that can be positioned by the user next to any desired group. The number of each type of subgroup in a given molecule could then be typed next to the appropriate subgroup ID on the screen. A menu selection for "Resume Program Execution" would be selected by the user only after the subgroup breakdown of the molecule is completely defined. While on the screen (before final selection), an entry could be changed at any time by the user. These and other useful improvements to the interactive software could not be implemented within the scope of the present contract.

B. FUTURE EXPERIMENTAL WORK

Because pure component vapor pressure data are necessary to calculate Henry's law constants from UNIFAC activity coefficients, additional experimental work should include the measurement of saturation pressures as necessary. For those compounds whose published Antoine constants do not apply at near-ambient "environmental" temperatures (or are not available), at least one saturation pressure measurement between 10 °C and 30 °C is recommended.

Experimental determination of Henry's law constants and aqueous solubilities should be designed to complement the thermodynamic modeling objectives. For instance, missing UNIFAC interaction parameters between subgroups can be used to logically select experiments that fill such data gaps. For this reason, future experiments should focus on oxygenated compounds and chemicals with multiple bonds (e.g., olefins). Such chemicals would be environmentally interesting in their own right and would increase the scope of the environmental UNIFAC database being developed.

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